U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-253 328

WATER QUALITY MONITORING IN DISTRIBUTION SYSTEMS

NATIONAL SANITATION FOUNDATION

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

MAY 1971

Library
Environmental Protection Agency
Washington, D. C. 20460

RESEARCH REPORT

PB 253 328

WATER QUALITY MONITORING IN DISTRIBUTION SYSTEMS

NATIONAL SANITATION FOUNDATION

ANN ARBOR, MICHIGAN

MAY 1971

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

161051

Library
Environmental Protection Agency
Washington, D. C. 20460

This report has been prepared for the Water Hygiene Division, Water Quality Office, Environmental Protection Agency in partial fulfillment of requirements for the project, "Water Quality Monitoring in Distribution Systems." The work described in this report was supported by Research Grants No. 1 R01 EC 00318-01 and -02. Progress during the continuation phase of this project will be described in a subsequent report prepared at the end of the current period of support.

PROJECT STAFF

Co-Principal Investigators

Robert M. Brown
President
National Sanitation Foundation
(Administrative Management)

and

K. H. Mancy, Ph.D.
Professor of Environmental Chemistry
The University of Michigan
(Research Operations)

Project Director

Nina I. McClelland, Ph.D.

Research Personnel

John R. Adams

Nabih P. Kelada

Thomas L. Schwenk

Farouq R. Shafie, Ph.D.

Secretary

Sue E. Buske

TECHNICAL ADVISORY COMMITTEE

Harry A. Faber, Chairman
Research Director
American Water Works Association
  Research Foundation
New York, New York

N. J. Davoust
Assistant Engineer
Water Purification Division
Department of Water and Sewers
Chicago, Illinois

T. E. Larson
Head, Chemistry Section
Illinois State Water Survey
Urbana, Illinois

Blucher A. Poole
Consultant
Indianapolis, Indiana

Joseph V. Radziul
Chief, Research & Development
Water Department
Philadelphia, Pennsylvania

Verdun Randolph
Assistant Chief Sanitary Engineer
Illinois Department of Health
Springfield, Illinois

Gordon G. Robeck
Assistant Director
Water Quality Office
Division of Water Hygiene
Environmental Protection Agency
Cincinnati, Ohio

T. L. VanderVelde
Assistant Chief, Engineering Section
Michigan Department of Public Health
Lansing, Michigan

Richard Woodward
Camp, Dresser, & McKee
Boston, Massachusetts

TABLE OF CONTENTS

Page

PROJECT STAFF ii

TECHNICAL ADVISORY COMMITTEE iii

LIST OF TABLES vii

LIST OF FIGURES ix

1.0 INTRODUCTION 1

- 1.1 Objectives 1
- 1.2 Methodology 1

2.0 ION SELECTIVE ELECTRODES 5

- 2.1 Theory 5
  - 2.11 Principle of Operation 5
  - 2.12 Primary Electrode Characteristics 7
  - 2.13 Secondary Electrode Characteristics 11
- 2.2 Equipment 15
- 2.3 Electrode Evaluations 16
  - 2.31 Hardness 16
    - 2.311 General 16
    - 2.312 Primary Electrode Characteristics 17
    - 2.313 Secondary Electrode Characteristics 24
    - 2.314 Feasibility for Potable Water Monitoring Applications 26
    - 2.315 Summary 33
  - 2.32 Nitrate 35
    - 2.321 General 35
    - 2.322 Primary Electrode Characteristics 35
    - 2.323 Secondary Electrode Characteristics 50
    - 2.324 Feasibility for Potable Water Monitoring Applications 54

2.33 Chloride 55

2.331 General 55
2.332 Primary Electrode Characteristics 55
2.333 Secondary Electrode Characteristics 58
2.334 Feasibility for Potable Water Monitoring Applications 59

2.34 Fluoride 60

3.0 CHARACTERIZATION OF CALCIUM CARBONATE SATURATION EQUILIBRIUM 99

3.1 General 99
3.2 Theory 99

3.21 Equilibrium Considerations 99
3.22 Kinetic Considerations 102

3.3 Experimental 104

3.4 Summary 124

4.0 CHARACTERIZATION OF TRACE METALS IN DRINKING WATER BY ANODIC STRIPPING VOLTAMMETRY 126

4.1 General 126
4.2 Theory 128
4.3 Experimental 132

4.31 Materials and Methods 132
4.32 Results and Discussion 137

4.4 Summary 140

5.0 GROSS ORGANICS 142

5.1 General 142
5.2 Theory 143
5.3 Experimental 144

5.31 Materials and Methods 144
5.32 Results and Discussion 145

5.4 Summary 156

6.0 RESIDUAL CHLORINE 158

- 6.1 General 158
- 6.2 Theory 159
- 6.3 Experimental 164
  - 6.31 Materials and Methods 164
  - 6.32 Results and Discussion 165
- 6.4 Summary 178

7.0 TURBIDITY 179

- 7.1 General 179
- 7.2 Theory 179
- 7.3 Experimental 180
  - 7.31 Materials and Methods 180
  - 7.32 Results and Discussion 183
- 7.4 Summary 184

8.0 FUTURE WORK 185

9.0 REFERENCES 187

ACKNOWLEDGEMENTS 190

LIST OF TABLES

TABLE:		Page
2-I	Percent Concentration Errors Due to Ionic Strength Changes	14
2-II	Selectivity Coefficients and Interferences	20
2-III	Long Term Stability of Divalent Cation Selective Electrode	23
2-IV	Percent of Calcium Sensed in Solutions Containing Various Amounts of Bicarbonate Alkalinity	27
2-V	Selectivity Coefficients for Various Interfering Ions	39
2-VI	Chloride Concentration Reductions with Various Ion Exchange Resins	45
2-VII	Equations Relating Ionic Strength and Nitrate Activity Coefficient	52
I*	OH^- Selectivity Coefficients (K)	72
II	Shift in Intercept of Calibration Curves at Low pH Values	76
III	Aluminum Complexing Effect and Fluoride Recovery by Different Masking Agents	81
IV	Iron Effect and Fluoride Recovery by Masking Agents	84
V	Characterization of Fluoride in Ann Arbor, Michigan Water Supply	90
3-I	Stability Index Monitor with Marble Chips in the Column	107
3-II	Stability Index Monitor with Powdered $CaCO_3$ in the Column	107
3-III	Analysis of Calcium Carbonate Equilibrium Experiment Test Solutions	113

*Tables I-V pertain to the paper on fluorides and do not follow the numbering format established for the other sections of the report (see Section 2.34).

3-IV Summary of Data from Analyses of Test Solutions 120

5-I UV Absorbances and TOC Determinations for Various Processed Waters 150

5-II Time Survey of UV Absorbances at 260 nm of Various Processed Waters 153

5-III Effect of pH on UV Absorption of Processed Water 154

LIST OF FIGURES

FIGURE:		Page
2-1	Total Ionic Strength vs. Activity Coefficient	12
2-2	Divalent Cation Electrode Response	18
2-3	Estimation of Total Ionic Strength from Conductivity Measurement	29
2-4	Total Ionic Strength vs. Activity Coefficient of Ca^{2+} (or Mg^{2+}) in Pure Solutions	30
2-5	Schematic Diagram of Apparatus for Monitoring of Water Hardness by the Automated Known Addition Technique	34
2-6	Typical Calibration Curve, $[NO_3^-]$ vs. mv	37
2-7	Nitrate Concentration vs. Chloride Selectivity Coefficient	41
2-8	Total Ionic Strength vs. Activity Coefficient; Approximation of Fig. 2-1 (on linear coordinates) by four straight lines	51
2-9	Chloride Calibration Curve	57
1*	Effect of pH on Fluoride Ion Selective Electrode Measurement	70
2	Calibration Curves at Different Levels of pH	73
3	Effect of pH on Fluoride Ion Electrode Sensitivity	77
4	Complexometric Titrations of Fluoride with Aluminum	79
5	Aluminum Complexing Effect and Fluoride Recovery by Different Masking Agents	82
6	Rate of Fluoride Recovery with Citrate	85
7	Rate of Fluoride Recovery with CDTA	86
8	Effect of Acetate Buffer on Free Fluoride Measurement	88

*Figures 1-10 pertain to the paper on fluorides and do not follow the numbering format established for the other sections of the report (see Section 2.34).

9 Schematic Illustration for Characterization of Fluorides in Drinking Water 89

10 Schematic Illustration of Free and Total Fluoride Monitor 92

3-1 Stability Index Monitor for Saturation Equilibrium Measurement 106

3-2 Distilled Water in Contact with Pure Powdered $CaCO_3$ 109

3-3 Distilled Water in Contact with Marble Chips 110

3-4 Ann Arbor Tap Water in Contact with Pure Powdered $CaCO_3$ 111

3-5 Ann Arbor Tap Water in Contact with Marble Chips 112

3-6 Current vs. Potential Sweep 118

3-7 CCDT: Effect of Initial Solution Composition on Rate of Film Formation 119

3-8 Correlation of CCDT Slope with Langelier Saturation Index 122

3-9 Correlation of CCDT Slope with Ryzner Stability Index 123

4-1 Typical ASV Voltammogram 131

4-2 Schematic Illustration of ASV Equipment 133

4-3 Anodic Stripping Voltammetric Cell 135

4-4 Diurnal Variations of Pb and Cu in Early Summer 138

4-5 Diurnal Variations of Pb and Cu in Late Summer 139

4-6 Distribution System Map Showing Sampling Sites 141

5-1 Schematic Illustration of Aqua Test Monitor Control Panel 146

5-2 Schematic Illustration of Aqua Test Monitor Detector Assembly 147

5-3 UV Scans of Various Processed Waters 148

5-4 UV Scans of One Processed Water with Varying Phenol Additions 151

6-1 Schematic of Capital Controls Residual Chlorine Analyzer 160

6-2 Sample Recorder Output of Capital Controls Analyzer 167

6-3 Potentiometric Titration of a Synthetic Chlorine Solution with Iodide 170

6-4 Potentiometric Titration of Tap Water with I^- 171

6-5 Potentiometric Titration of Chlorine - Spiked Tap Water with I^- 172

6-6 Potentiometric Titration of Chlorine - Spiked Tap Water + NH_4OH with I^- 173

6-7 Ion Selective Electrode Method - % Standard in Solution vs. $[Cl_2]$ 175

6-8 Flow System for Automation of Ion Selective Electrode Method 176

7-1 Cut-Away View of the Hack CR Low Range Turbidimeter Model 1720 181

7-2 Schematic of Turbidimeter-Bubble Trap Assembly 182

1.0 INTRODUCTION

1.1 OBJECTIVES

The overall objective of this project is to develop basic scientific criteria and specifications for a continuous monitoring system for use in the detection and control of water quality deterioration in distribution systems, and in quality control of water purification processes. Specific aims include: (1) developing new sensor systems, (2) establishing the analytical feasibility of commercially available sensors for potable water quality monitoring applications, and (3) evaluating under laboratory and field conditions the performance characteristics of each sensor in the system.

1.2 METHODOLOGY

Project priorities, currently in various stages of completion, were established at the first meeting of the Technical Advisory Committee:

- Evaluate the performance characteristics of commercially available ion selective electrodes - specifically fluoride (F^-), nitrate (NO_3^-), chloride (Cl^-), and divalent cation (Ca^{2+}, Mg^{2+} ...$^{2+}$) selective electrodes - and establish the analytical feasibility of each for potable water quality monitoring applications.

- Develop methodology for the continuous measurement of calcium carbonate ($CaCO_3$) stability and corrosivity.
- Develop a system for measuring trace metals - specifically copper (Cu), lead (Pb), cadmium (Cd), and zinc (Zn).
- Develop techniques for continuously monitoring alkalinity [Alk], aluminum (Al), phosphates (PO_4), and gross organics.
- Evaluate corollary relationships between residual chlorine, turbidity and iron (Fe) measurements and coliform organism densities.

Equipment acquisitions include:

- Complete Heath/Malmstadt-Enke electronics instrumentation laboratory with full capabilities for electroanalytical analysis and circuit design. Components include a universal power supply, a voltage reference source, an operational amplifier system, two multi-speed servo chart recorders, a DC oscilloscope, a sine and square wave generator, and resistance and capacitance substitution boxes.
- Heath log/linear current recording system which functions as a recording photometer or as a

picoammeter for micro current applications.

- Heath/Malmstadt-Enke "701" modular UV-visible single-beam spectrophotometer. This instrument is designed to permit integration of the monochrometer and photomultiplier components with other modules, expanding its capability to include atomic absorption, atomic fluorescence, flame emission, and double beam systems.
- Orion Model 801 digital pH/mv meter designed for use with specific ion, pH or redox electrodes. The binary coded decimal output from this instrument makes data available for interfacing with computers, controllers, titrators, printers, magnetic data recorders, or card or tape punchers.
- Orion six channel automatic or manual electrode switch that provides the capability for monitoring simultaneously the activities of up to six ions in a single solution or in different solutions.
- pH, single and double junction reference, and ion activity electrodes specific for Cd, Cl, Cu, F, Pb, NO_3, and hardness.
- Mettler H20T semi-micro analytical balance with digital readout.
- YSI (Yellow Springs Instrument Co.) Model 31 direct reading conductivity bridge.

- Haake Model FS constant temperature circulator.
- Rotating ring disc electrode assembly, consisting of an RDE-1 rotating ring disc electrode, and a PIR rotator.
- Honeywell Electronik 194 multi-speed, multi-range electronics strip chart recorder.
- Corning Model 101 digital pH-mv meter.

Additional field and laboratory instrumentation has been consigned to NSF by a number of manufacturers for use on the Water Quality Monitoring Project:

- Schneider Instrument Model RM 25 Robot Monitor, Schneider Instrument Company.
- Capital Controls Residual Chlorine Analyzer, Model 871, Capital Controls Company, Inc.
- Aqua Test Water Quality Monitor for gross organics, Aqua Test Corporation.
- Hach Continuous Flow Low Range Turbidimeter, Model 1720, Hach Chemical Company.
- Corning Model 112 digital pH/mv meter, numerous selective ion electrodes, and an Orion Model 851 digital printer, Van Waters and Rogers Scientific Co.
- Wallace and Tiernan Amperometric Titrator, Model A-790, City of Chicago.

2.0 ION SELECTIVE ELECTRODES

2.1 THEORY

2.11 Principle of Operation

Electrodes which are sensitive to a particular ion or class of ions to the exclusion of most other ions are commonly referred to as "ion selective electrodes." These electrodes respond to potential differences created by the movement of ions across a membrane. The mechanism by which an ion passes through - or is excluded from - a membrane is discussed in detail by Eisenman,[1] and considered briefly under the heading "*Selectivity*" in this report.

Potentiometric membrane ion selective electrodes can be used to measure the activities of those ions for which selective membranes have been discovered. Many such membranes are known; however, there are only two basic types: liquid ion exchanger and solid ion exchanger. In the former type, a high molecular weight organic liquid which has the capacity to solubilize only the ion of interest into the membrane phase forms the solution interface across which the difference in activities of a specific ion causes a potential difference. The membrane of solid ion exchanger electrodes consists "simply" of a solid crystal of a sparingly soluble salt of the ion of interest.

The response of an ion selective electrode is described by a modified form of the classical Nernst equation:

$$E_{meas} = E_{const} + \frac{RT}{Z_A F}\ [\ln\ (\gamma_A C_A + \Sigma\ k_i \gamma_i C_i^{\ Z_A/Z_i})] \qquad (2.1)$$

where:

E_{meas} = measured electrode potential

E_{const} = a constant potential characteristic of the indicator-reference electrode couple

R = gas constant

T = absolute temperature of the test solution

F = the Faraday

Z_A = ionic charge of the ion of interest

γ_A = activity coefficient of the ion of interest

C_A = analytical concentration of the ion of interest

k_i = selectivity coefficient of the i^{th} interfering ion

γ_i = activity coefficient of the i^{th} interfering ion

C_i = analytical concentration of the i^{th} interfering ion, and

Z_i = ionic charge of i^{th} interfering ion

The response curve, drawn on semilogarithmic paper, is a straight line with its slope equal to $\frac{RT}{Z_A F}$. Ideally, the sign and magnitude of the slope depends on Z_A at constant temperature. For a ten fold variation in ion activity the slope at 25°C. for various ion classes is as follows:

monovalent anion = -59.15 mv
divalent anion = -29.58 mv
monovalent cation = $+59.15$ mv
divalent cation = $+29.58$ mv

2.12 Primary Electrode Characteristics

Primary electrode characteristics are those which are a function of electrode design and are independent of the environment in which it is used. They include: (1) sensitivity, (2) selectivity, (3) accuracy and precision, and (4) long term stability.

Sensitivity

The absolute sensitivity of any ion selective electrode is a function of the solubility of the ion exchanger - the greater the solubility product of the exchanger matrix, the greater the sensitivity of the electrode. This is clearly illustrated by the response curve of any ion selective electrode. As the activity of the analate ion decreases, the response is a straight line to a point, then begins to taper off to a constant value regardless of the activity of the bulk solution. The tapering is a result of the increasing contribution of the analate ion which is dissolved at the surface of the membrane, limiting the lower limits of detection.

Selectivity

"Selectivity" of the sensor refers to the effect of interferences resulting from detectable ions or molecules other than the species of interest. Because all sensor systems cannot achieve absolute (100%) selectivity, it is important to specify selectivity limitations in a test solution. If the type and amount of the interfering species are known, it is possible to incorporate the term "selectivity coefficient" in Equation (2.1). The terms $\gamma_A C_A$ and $\gamma_i C_i$ refer to activity levels of the ion being measured and interfering ion, respectively, in the test solution. The activity of each interfering ion in the test solution, raised to a power equal to the charge ratio (Z_A/Z_i), is multiplied by the correction factor, or selectivity coefficient k_i.

In general, the selectivity of a membrane system for one ion over another depends upon two factors: 1) the relative mobility of the two ions through the membrane, and 2) the ion exchange equilibrium constant of each ion with the ion exchange solution.[1] In solid state electrodes, a highly selective crystalline disc serves as the electrode membrane. Conduction of ions through the crystal lattice by a lattice defect mechanism is controlled by ion size, shape and charge. It is possible to select crystal membranes which are very specific in the type of vacancy caused by the defect, and thus so selective that only one particular ion can travel through the lattice. Thus, the selectivity of solid state electrodes is a function of controlling the first factor of selectivity.

In liquid junction electrodes, the membrane is used merely to separate the sample and the liquid ion exchanger. It is equally permeable to all ions. The selectivity of the electrode is a function of differences in ion exchange equilibrium constants; thus, it cannot be controlled as it is in solid state electrodes. The electrode senses, to various degrees, ions other than the ion of interest. This problem with ion interferences is amplified in non-controllable situations, such as tap water monitoring, where the ionic content of the water is complex and often unknown.

Accuracy and Precision

The "accuracy" of any sensor system is defined by the extent of deviation from "true" value. If the source of error is found and correction can be made, this is "determinate error." If the deviation from true value is compounded indiscriminately by many small errors, it is simply a "random error." Random errors are subject to statistical treatment of the data.

"Precision" is defined in terms of reproducibility of the sensor measurement. The more scatter in successive readings, the less precise are the measurements. In general, precision is closely identified with random errors and statistical theories.

An important distinction between precision and accuracy is that accurate measurements are always precise, but the converse is not necessarily true. The precision of a series of measurements may be good, but every result may be higher than the true value because of an unsuspected interference. Only when determinate errors are minimized will precision also imply accuracy.

Electrode potential measurement is, although not a characteristic of the electrode, an important factor. Measurement of the potential to the nearest 0.1 mv will yield a relative error of 0.4% or 0.8% for monovalent and divalent electrodes, respectively. A 1.0 mv error in measurement increases the error to 4% and 8%. Clearly, electrode potential must be measured with the greatest accuracy possible.

Long Term Stability

"Long term stability" usually refers to change in a sensor's performance characteristics with time. This characteristic of the sensor affects the frequency at which it must be calibrated and serviced. A sensor which displays a gradual cumulative drift must be calibrated frequently; a sensor which is known to be stable requires less frequent calibration. This kind of drift refers to shifting of the entire calibration curve.

A second kind of drift, variation of the slope, is generally related to deterioration of the membrane and limits the useful service life of the electrode. There is a marked difference between liquid and solid junction sensors. In general, liquid junction electrodes must be rejuvenated at more frequent intervals - on the order of once each month. Solid state electrodes do not display this kind of drift until they are approaching the end of their useful life, at which time they must be replaced or returned to the manufacturer for expert rejuvenation.

2.13 Secondary Electrode Characteristics

Secondary electrode characteristics are those which are a function of environmental variables: (1) ionic strength, (2) temperature, and (3) pH.

Ionic Strength

Disregarding the effects of interfering ions, two solutions having equal concentrations of the ion of interest but significantly different total ionic strengths (μ) will show different ion activities by the electrode. This is because activity is related to concentration by the activity coefficient which is dependent on total ionic strength (Fig. 2-1). Fig. 2-1 is for monovalent anions and is predicted by Debye-Huckel theory.[2]

In working with solutions in which ions other than the one of interest contribute to ionic strength, the ionic strength of the sample must be known before accurate calibrations can be made. If a calibration curve made at

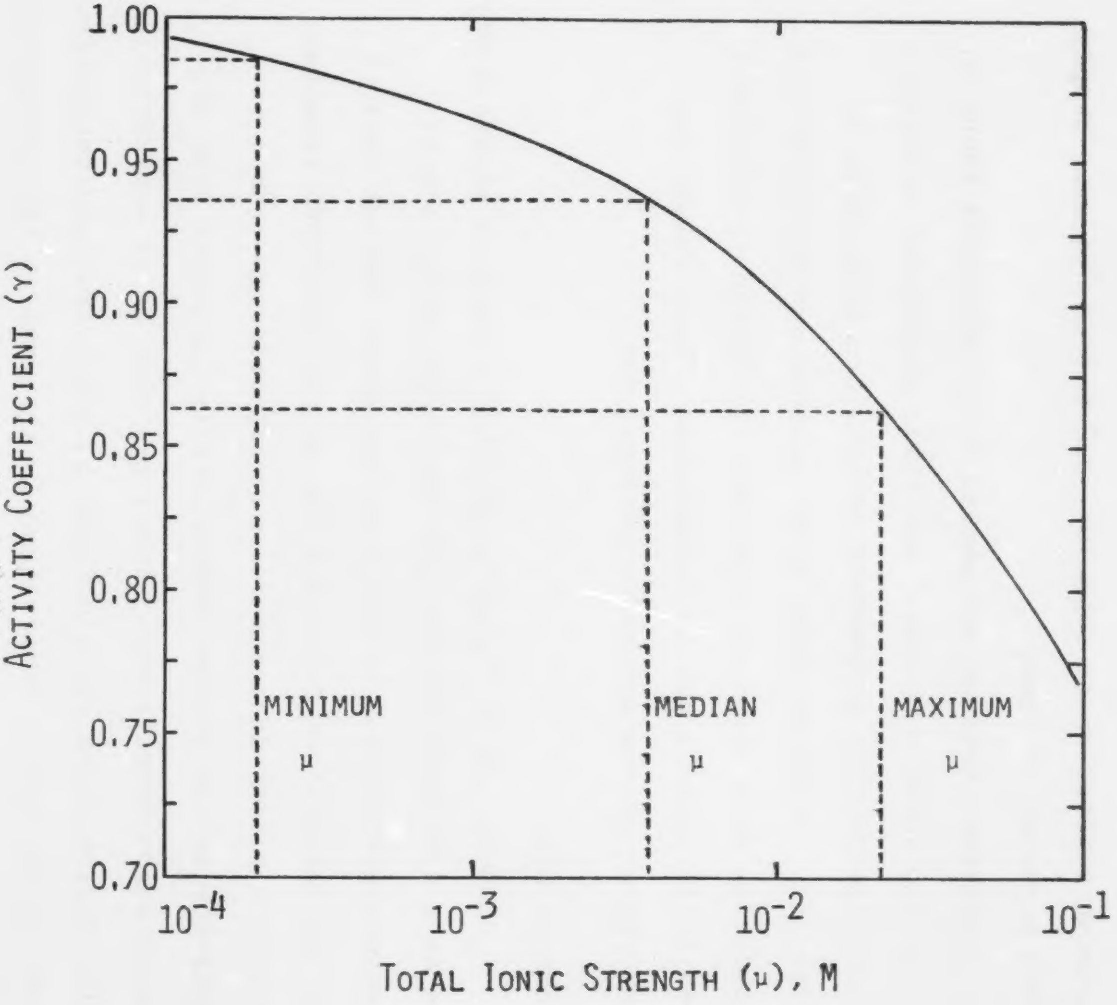


FIGURE 2-1. TOTAL IONIC STRENGTH VERSUS ACTIVITY COEFFICIENT

one ionic strength were used to determine ion activity in a solution of totally different ionic strength, a large error could result from differences in the activity coefficients. This problem is significant in monitoring situations where large variations in ionic strength exist between various water supplies, and within the same supply over a period of time.

Minimum, maximum and median ionic strengths found in U. S. tap water supplies,[3] and their associated activity coefficients, for monovalent anions, are also shown in Fig. 2-1. Based on these data, maximum and median errors resulting from using an incorrect calibration curve for a particular sample can be calculated. These values for monovalent anions are shown in Table 2-I.

Temperature

Because the electrode's internal reference standard may be at a different temperature than that of the sample, temperature changes affect both the slope (Nernst factor) of the calibration curve and the actual electrode response. Measured electrode potential may not indicate true ion activity if the sample temperature is different from the calibration temperature. There may also be an equilibration time during which the electrode is not responding correctly, even if the sample temperature is the same as the calibration temperature. This may result from the internal reference solution's being at a totally different temperature because

TABLE 2-I

PERCENT CONCENTRATION ERRORS DUE TO IONIC STRENGTH CHANGES

Ionic Strength Used For Calibration Curve	Ionic Strength of Unknown Sample	Error
2×10^{-4}M (minimum)	2.2×10^{-2} (maximum)	13.10%
3.8×10^{-3}M (median)	2×10^{-4} (minimum)	5.00%
3.8×10^{-3}M (median)	2.2×10^{-2} (maximum)	8.10%

of previous immersions in solutions of different temperatures.

pH

The sample pH can have a number of effects on electrode response, depending upon the electrode being used. At high pH, OH^- may be partially sensed by monovalent anion electrodes. This effect is described under "*Selectivity*". At low pH, H^+ may complex the ion to be measured, making the ion unavailable for measurement by ion activity sensors. At very low pH, the sample may attack the electrode body and membrane assembly, resulting in permanent deterioration.

2.2 EQUIPMENT

Equipment used in evaluating the performance characteristics of ion selective electrodes described in this report included the following items:

- Electrodes
    - Orion 92-32 (divalent cations)
    - Orion 92-07 (NO_3^-)
    - Orion 92-17, 94-17, and 94-17A (Cl^-)
    - Beckman 41263 (H^+)
    - Orion 90-01 and 90-02 (reference)
    - Corning 476-022 (reference)
- Digital pH/mv meters
    - Orion 801
    - Corning 101 and 112

- Electrode switch
  Orion 855
- Magnetic stirrer
  Corning PC-353
- Recorder
  Heath EU-20B
- Spectrophotometer
  Heath 701

Ion exchange resins used for selectivity experiments were strongly acidic cation exchange resins of the styrene divinyl-benzene co-polymer type with sulfonic acid functional groups, manufactured by Dow Chemical Company and Mallinckrodt Chemical Works. All chemicals were analytical reagent grade.

2.3 ELECTRODE EVALUATIONS

2.31 HARDNESS

2.311 General

The term "water hardness" has had several definitions over the years, some of which have had little meaning. In England in 1856, Thomas Clark reported, "Each degree of hardness is as much as a grain of chalk or the calcium in a grain of chalk would produce in a gallon of water, by whatsoever means dissolved."[4] Another definition, widely used in the twentieth century, defines hardness as, "a property of water that is the measure of the amount of soap that is required to form a lather."[5] This "practical definition" led to a method which was for many years accepted as the standard method for determining water hardness. The introduction of ethylenediaminetetraacetic acid (EDTA) and sensitive endpoint indicators provided a quantitative technique which is now the standard method for measuring water hardness. More recently, development of the divalent cation selective electrode has provided a new analytical tool for measuring the hardness of water.

Interest in water hardness, which is now defined as, "the sum of the concentrations of divalent metal ions (Ca, Mg, Sr, Fe, Al, Zn, and Mn), expressed as mg/liter of equivalent calcium carbonate,"[5] has grown in this century with the increased use of iron pipe in distribution systems serving millions of persons, and high temperature and pressure reaction vessels and cooling systems in industry. Calcium carbonate has the capacity to form a very hard, difficult to remove scale on the surface of pipelines. This scale can significantly reduce the effective carrying capacity of pipes.

2.312 Primary Electrode Characteristics

Sensitivity

Electrode response, as shown in Fig. 2-2, is linear when plotted on semilogarithmic paper. The point at which the line begins to taper off indicates the limit of

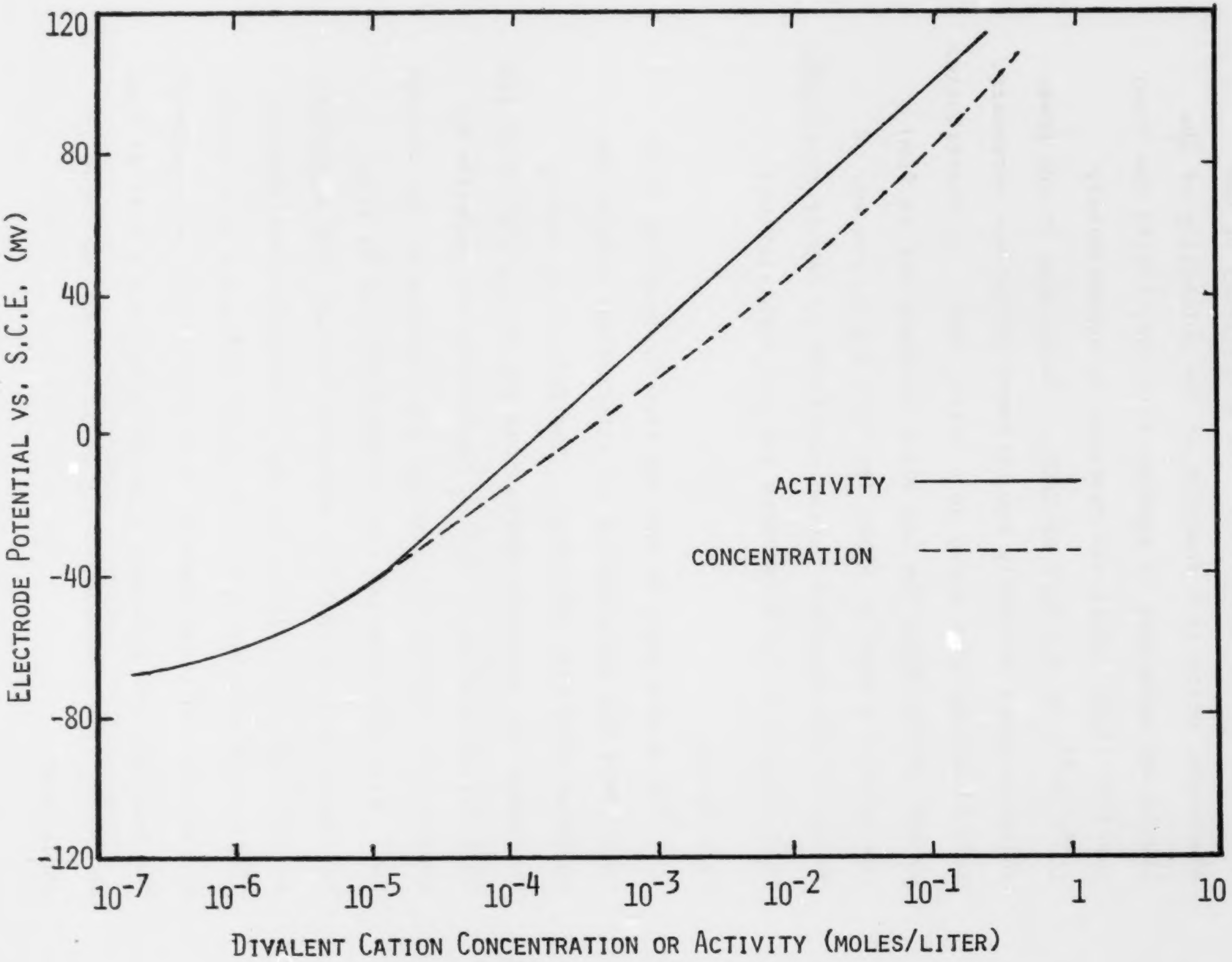


FIGURE 2-2. DIVALENT CATION ELECTRODE RESPONSE

detection of the electrode. The sensitivity of the electrode, which is a function of the solubility of the liquid ion exchanger in aqueous solution, limits the lower level of linear electrode response to approximately 10^{-6}M Ca^{2+}, or 0.1 mg/l as $CaCO_3$. Thus, even in the power industry where extremely low hardness waters are necessary, this electrode will serve as a useful tool. In distribution system waters where the tap water hardness varies from a low of 0 to a high of about 740 mg/l and an average of 90 mg/l,[3] the divalent cation electrode is easily applicable with respect to interferences and ion complexations.

Selectivity

The second part of the log term in Equation (2.1) represents the contribution of interfering ions to the measured electrode potential. The factors γ_i and C_i represent the activity coefficient and concentration of the interfering species i, and k_i represents the selectivity coefficient for the interfering ion relative to the desired ion. With the divalent cation electrode, it is also necessary to note that the membrane has somewhat different selectivity coefficients for the various divalent cations. If divalent cations of significantly different selectivity are present in large levels, this effect must be considered. The manufacturer provides with the electrode a list of ions and their relative selectivity coefficients, as shown in Table 2-II.

TABLE 2-II

SELECTIVITY COEFFICIENTS AND INTERFERENCES[6]

Approximate Divalent Cation Selectivity Coefficients (pH=6)

Divalent Cation	Selectivity Coefficient	Divalent Cation	Selectivity Coefficient
Zn	3.5	Ca	1.0
Fe	3.5	Mg	1.0
Cu	3.1	Ba	0.94
Ni	1.35	Sr	0.54

- The electrode responds positively to Na^+ (k = 0.15) and K^+ (k<0.1)
- For measurements below 10^{-4}M Ca^{2+}, the pH must be over 7. For solutions as concentrated as 10^{-1}M Ca^{2+}, the pH must be greater than 5.

Accuracy and Precision

The slope for the electrode response to divalent cation activity is relatively small and limits the accuracy of measurements to about 4% under normal operating conditions, or 0.4% under strictly controlled conditions and very accurate potential measurements in the laboratory. Another consideration, typical of any logarithmic response device, is the inability of the electrode to respond to small variations in activity at high concentrations; but this is not a serious problem with hardness measurements. Conversely, the logarithmic device is extremely sensitive to small changes at lower levels of activity and, as a result, becomes even more useful as a device for hardness monitoring in boiler works applications where small changes in water hardness are important.

Another important aspect of the accuracy of divalent cation electrode measurements is determination of the activity coefficient for divalent cations in the test solution. As stated previously, ion selective electrodes respond only to the activity of the ion of interest rather than directly to the concentration of that ion, according to the relationship $a = \gamma C$, where "a" is the thermodynamic activity, "γ" is the activity coefficient, and "C" is the total concentration of the ionic species in solution. In theory the activity of an ion is equal to the concentration of an ion only at infinite dilution; thus, when attempting to make concentration measurements with an ion selective electrode, the activity coefficient of the ion must be determined before a meaningful interpretation of the measurement can be made. The activity of an ion is defined by the total ionic strength of the test solution. With the total ionic strength established, either by calculation or by estimation from a graph of total ionic strength versus electrical conductivity of the test solution, the activity coefficient can be determined from a graph of activity coefficient versus total ionic strength. Because of its relative simplicity and observed accuracy, the estimation of total ionic strength from measurements of electrical conductivity was the preferred method in this study. An example of this technique is given in Section 2.314 of this report, along with another technique which required no direct knowledge of the activity coefficient.

Long Term Stability

For a sensor to be useful in a monitoring system, it must be relatively free of drift without frequent recalibration over reasonably long periods of time, and physically stable without rejuvenation or replacement. The two divalent cation electrodes used in this study which meet these requirements quite satisfactorily, show no signs of physical wear after 18 months of use. Long term electrical response of both electrodes is characterized by the data in Table 2-III, summarizing median and extreme

TABLE 2-III

LONG TERM STABILITY OF DIVALENT CATION SELECTIVE ELECTRODE

E_{meas} vs. S.C.E., (mv)	$1.0 \times 10^{-4}M$	$1.0 \times 10^{-3}M$	Slope
Lowest	-48.5	-21.3	22.4
Highest	-13.6	+10.9	31.6
Median	-29.4	- 3.8	25.6

potential measurements taken with the electrodes in 1.0×10^{-4}M and 1.0×10^{-3}M solutions of $CaCl_2$. These were the solutions used to calibrate for hardness measurements in Ann Arbor, Michigan tap water. These figures are potential measurements which were taken with both electrodes and represent fourteen different rejuvenations of the electrodes. Variation in the slope of the electrode is not desirable, and a sensor which displays variations in its response to changes in the parameter it is designed to measure is to be avoided. Data shown in the table do not indicate such variation, but do vary as a result of different rejuvenations.

Variation in the slope of electrode response over a long period of time was carefully observed. The initial slope of the electrode was 25.6 mv per ten fold change in divalent cation activity. Measurements taken over the next 38 days showed only a very slow cumulative decay. After 38 days, the electrode slope was 24.5 mv per decade. This decay of the slope accelerates quite rapidly toward the end of the useful life of a particular rejuvenation period. In field applications, monthly rejuvenation of the probe appears advisable. The time required for rejuvenation is less than thirty minutes.

2.313 Secondary Electrode Characteristics

Ionic Strength

Conductivity variations in the order of ± 100 μmho/cm result in less than 3% change in activity coefficients for divalent cation measurements.

Temperature

Because the slope of divalent cation electrode response is only half that of monovalent electrodes, small changes in temperature do not affect electrode response significantly.

pH

The pH of the sample is not important when the divalent cation electrode is considered for use in potable water applications. Cation type electrodes respond to H^+, but because potable waters are normally higher than pH 7, there is little reason to be concerned with the effects of low pH. Although the electrode does not respond to hydroxyl ion, high pH results in inaccurate measurements because of complexation of Mg^{2+}. Bicarbonate complexation at higher pH levels is also discussed in "*Complexation*."

Complexation

Complexation of the ion of interest is perhaps the most significant consideration in using ion selective electrodes to measure water quality parameters. In any distribution system water, there are ions present which will form soluble complexes with calcium and magnesium ions, masking these ions from the electrode. Examples of such complexes are $CaHCO_3^+$, $Mg(OH)^+$, various phosphate complexes, and so on.

An experiment was designed to determine the extent of complexation of calcium ion in waters of varying alkalinity. Six solutions of calcium chloride and sodium bicarbonate varying in concentration from 0 to 200 mg/l were used, a total of thirty six solutions of varying, but known, hardness and alkalinity. Percent recovery of free calcium as measured with the divalent cation electrode is a measure of the amount of calcium which has been complexed by bicarbonate ion. Table 2-IV shows the results of this experiment. From these data it is clear that the alkalinity of a particular water has varying effects on the availability of calcium to the electrode for sensing. A technique must be used which will make all of the calcium and magnesium available for sensing. Techniques which perform this function are described in the following section.

2.314 Feasibility for Potable Water Monitoring Applications

Selection of a method to be used for monitoring water hardness with the divalent cation electrode depends on several factors: (1) the nature of the tap water sample, (2) the degree of accuracy required, and (3) economics. If the sample is reasonably free from interferences, low in complexing agents, and extreme accuracy is not required, direct potentiometry is satisfactory. If a large excess of complexing agents is present, the sample pH is high, or a greater degree of accuracy is required, known addition

TABLE 2-IV

PERCENT OF CALCIUM SENSED IN SOLUTIONS CONTAINING VARIOUS AMOUNTS OF BICARBONATE ALKALINITY

	$NaHCO_3$, M									
	1.59×10^{-4}		7.94×10^{-4}		1.27×10^{-3}		1.59×10^{-3}		3.17×10^{-3}	
$CaCl_2$, M	Recovered, %	Soln. pH	Recov., %	Soln. pH	Recov., %	Soln. pH	Recov., %	Soln. pH	Recov., %	Soln. pH
2.0×10^{-3}	95.0	7.32	94.5	8.09	86.0	8.25	85.5	8.34	80.1	8.49
1.0×10^{-3}	91.0	7.30	86.2	8.16	83.0	8.35	84.0	8.41	80.0	8.50
7.0×10^{-4}	90.7	7.35	83.7	8.17	76.5	8.39	82.8	8.49	82.8	8.58
5.0×10^{-4}	88.0	7.33	83.0	8.20	74.0	8.43	81.0	8.50	81.0	8.65
2.0×10^{-4}	66.0	7.38	42.0	8.19	35.0	8.47	59.4	8.58	63.5	8.72
1.0×10^{-4}	49.1	7.37	38.5	8.26	10.6	8.64	57.0	8.60	53.1	8.74

differential potentiometry should be the method of choice.

Direct potentiometry is the simplest and least expensive technique which can be used; and, with a few reasonable assumptions and correction factors, is satisfactory for many applications. If, for example, water in the distribution system contains 50 mg/l (7.94×10^{-4}M) of alkalinity as HCO_3^-, and 100 mg/l of hardness as $CaCO_3$ (1.0×10^{-3}M Ca^{2+}), reference to Table 2-IV indicates that only about 86% of the hardness producing ions will be available for sensing by the divalent cation electrode. If the pH is higher than 8.5, even less will be available as a result of complexation of Ca^{2+} and Mg^{2+} with OH^-. If the pH and alkalinity are reasonably constant with time, an appropriate correction factor can be applied. If, in the same water, the electrical conductivity is 400 μmho/cm, total ionic strength of the sample can be determined from Fig. 2-3 (5×10^{-3}M) and from Fig. 2-4 an activity coefficient for divalent cations of 0.75 is found. For conductivities from 300 μmho/cm to 500 μmho/cm, the activity coefficient is 0.75 ± 0.02. Thus, the method used for monitoring hardness in this water involves calibration of the electrode in solutions of 1.0×10^{-4}M and 1.0×10^{-3}M $CaCl_2$ and comparison of the potential in tap water with a calibration curve. Application of the correction factors for complexation and activity coefficient will provide a reasonably accurate indication of the water hardness.

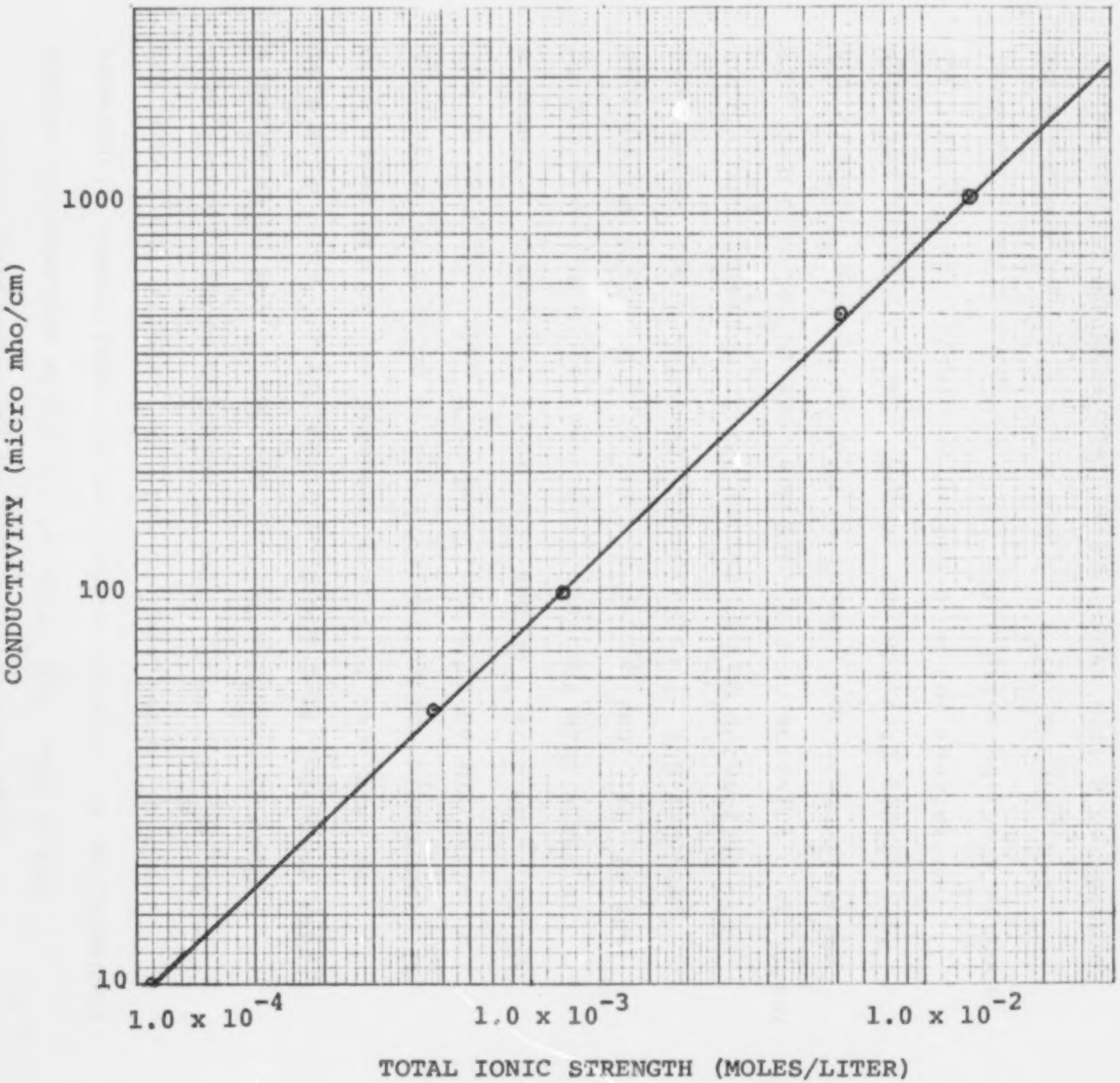


Figure 2-3. Estimation of total ionic strength from conductivity measurement

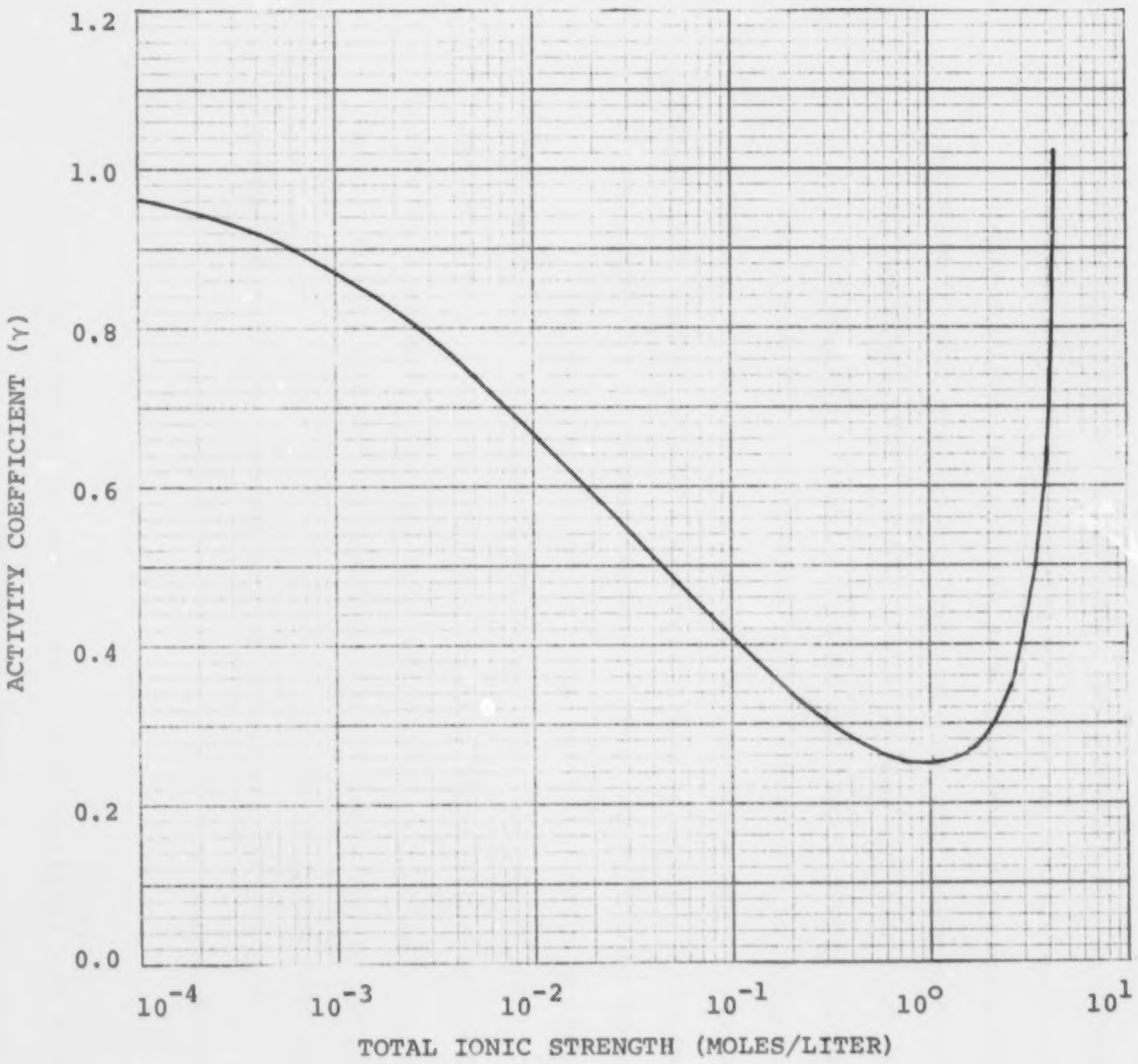


Figure 2-4. Total ionic strength vs. activity coefficient of Ca^{2+} (or Mg^{2+}) in pure solutions

The second method, the known reagent addition with differential potentiometry technique, is useful when complexing agents are present in excess, or the sample pH is high. This technique measures total water hardness concentration directly and requires no correction factors for complexation or activity errors. To be applicable, the sample plus addition must satisfy two requirements: (1) the added ions must be complexed in the same proportion as the addition, and (2) the activity coefficient of the ion of interest must not be significantly changed by addition of the reagent. For convenience and increased accuracy, the addition should be large enough to produce a potential change of sufficient magnitude to reduce statistical error to a minimum, and its volume should be sufficiently small to eliminate the need for volume correction.

The known addition technique is based on the principle that the addition of a known quantity of the ion of interest to a solution containing the same ion will produce a potential change proportional to the quantity of the ion in the unknown and the amount added.

The initial potential in the unknown solution is given by the equation:

$$E_1 = \text{const} + S \log C_o \qquad (2.2)$$

Upon the addition of a known volume of reagent of known concentration the potential becomes:

$$E_2 = \text{const} + S \log \left(\frac{C_o V_o}{V_o + V_s} + \frac{C_s V_s}{V_o + V_s}\right) \qquad (2.3)$$

and the potential change is:

$$E_2 - E_1 = \Delta E = S \log \left(\frac{V_o}{V_o + V_s} + \frac{{}^{C_s}/C_o \cdot V_s}{V_o + V_s}\right) \qquad (2.4)$$

Rearranging the equation:

$$C_o/C_s = \frac{(V_s/V_o)}{(1 + V_s/V_o)(10^{\Delta E/s} + 1)} \qquad (2.5)$$

If V_s/V_o is small (≈0.01), then:

$$C_o/C_s = \frac{0.01}{(10^{\Delta E/s} + 1)} \qquad (2.6)$$

and

$$C_o/C_s \cdot C_s = C_o \qquad (2.7)$$

where:

C_o = total concentration of the ion in the test solution

V_o = volume of the test solution

C_s = concentration of the standard addition

V_s = volume of the standard addition

S = observed slope of the electrode

If V_o, C_s, and V_s are carefully controlled and S and ΔE are measured with 0.1 mv accuracy, this technique becomes extremely accurate. Automation of this technique into a system which is capable of monitoring small changes in the hardness of distribution system waters involves precise proportioning of sample to reagent volume in the ratio of 100:1, and accurate measurement of the potential difference, ΔE. The arrangement of such a system, as shown in Fig. 2-5, involves the use of reagent and sample proportioning pumps and a dual high input impedence differential potentiometer.[7] For a well defined system, a direct readout of ΔE in units of water hardness is possible.

2.315 Summary

The Orion divalent cation electrodes used in this study provided accurate continuous measurements of water hardness, whether by direct potentiometry or by differential potentiometry with the known addition technique. The long term stability which is required of any sensor used in a continuous measurement system was demonstrated. The sensitivity of the probe is sufficient to make it useful even in the lowest hardness waters, as demonstrated by Oliver and Mannion[8] in monitoring the hardness of ion exchange treated cooling waters. In general, sodium is the only ion present in tap water which could cause a significant error, but with its low selectivity coefficient (0.15) -- and because the sodium concentration in distribution system waters is usually controlled at a low level to avoid the

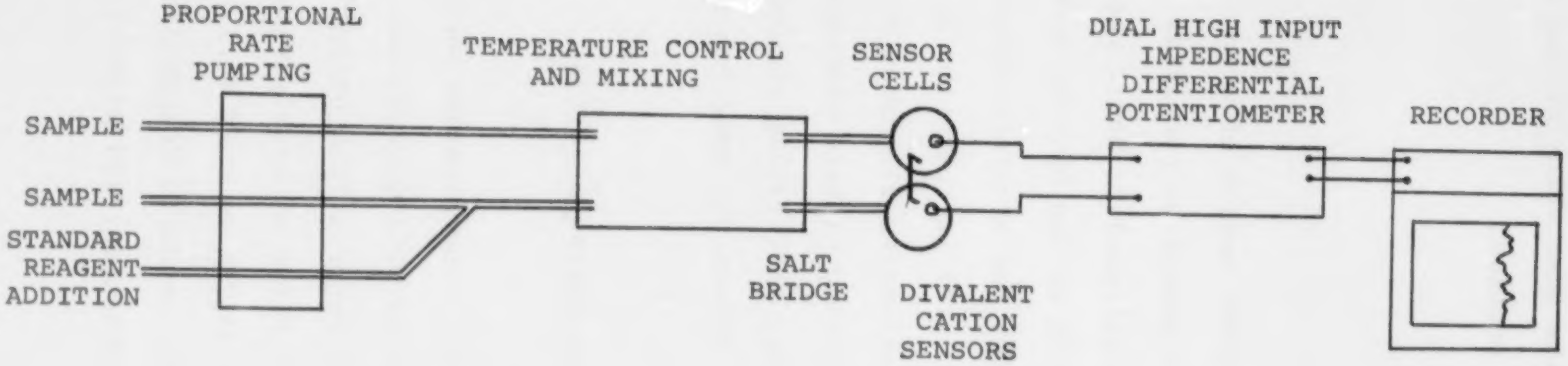


Figure 2-5. Schematic diagram of apparatus for monitoring of water hardness by the automated known addition technique

salty taste which results when chloride ion is also present -- it is not considered a problem.

2.32 NITRATE

2.321 General

Long- and short-term health effects and the maximum level of nitrates which should be permitted in drinking waters are not well established.[9] Until recently, only wet chemical methods such as the brucine and phenoldisulfonic acid methods[5] existed for the accurate determination of nitrate concentrations. The introduction by Orion Research, Inc. of a nitrate ion selective electrode has greatly improved the capability for measuring nitrate concentrations instantly and continuously, without sacrificing accuracy. The electrode method offers numerous advantages over the more conventional wet chemical techniques.

2.322 Primary Electrode Characteristics

Sensitivity

The range of nitrate concentration which can be effectively and accurately measured is well documented. Data obtained in this study substantiate reports from Orion[10] and Potterton and Shults[11], i.e., the range of sensitivity is from $1 \times 10^{-1}M$ to $1 \times 10^{-5}M$ (6,200 to 0.62 mg/l as NO_3^-). Above the upper limit, the electrode is responsive, but in a non-theoretical (non-Nernstian) and unpredictable manner.

From approximately 10^{-4}M to 10^{-5}M, the response curve levels off from the linear Nernstian response (Fig. 2-6) to a constant potential for all concentrations below 10^{-5}M. This curve is consistent and predictable, however, so it constitutes a useful portion of the range of sensitivity.

The median nitrate concentration of U.S. tap waters, according to the U.S. Geological Survey (USGS)[3], is approximately 0.7 mg/l. With a lower limit of sensitivity of about 0.6 mg/l, the electrode is capable of sensing nitrate in approximately half of all tap water supplies. However, knowledge of the exact nitrate concentration at levels of 0.6 mg/l or below may not be necessary, according to present information on the health effects of nitrate at this concentration.[9] The electrode responds the same for all waters at or below about 0.6 mg/l nitrate, as shown in Fig. 2-6, and this response is sufficient. The electrode's upper limit of detection is well above nitrate concentrations found in any supply of drinking water, thus no problem exists for the upper concentration limit.

Selectivity

As stated previously, liquid junction electrodes in general are subject to many more interferences than solid state electrodes, and the nitrate electrode is no exception. In monitoring tap water, where the sample composition is complex and unknown, errors caused by the electrode's partial sensing of other ions are serious.

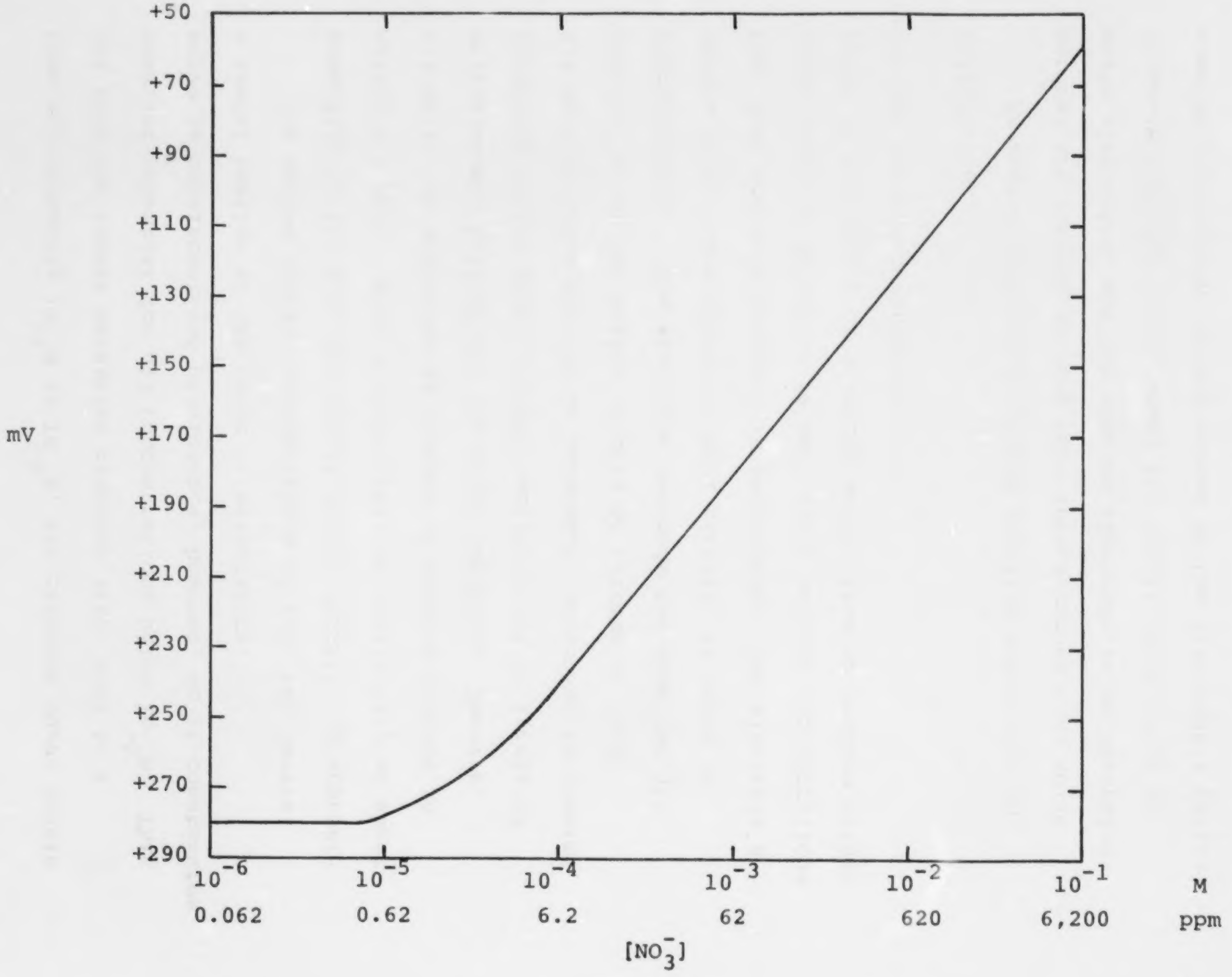


Figure 2-6. **Typical** calibration curve, $[NO_3^-]$ vs. mv

Selectivity constants were calculated and published by Orion[10], substantiated by Potterton and Shults[11], and questioned by Langmuir and Jacobsen.[12] Selectivity constants for various ions are shown in Table 2-V.[10] Potterton and Shults[11] calculated some of these constants and reported them to be somewhat higher for Cl^- and NO_2^-. Langmuir and Jacobsen[12], however, showed that the selectivity constants are not really constants at all, but rather vary in an unknown manner with the nitrate concentration. Also, the varying values given for Cl^- by Langmuir[12] _et al_ are as much as 5 times that which is stated by Orion.[10]

In this study, data were obtained which supported the evidence of Langmuir[12] _et al_ that the selectivity coefficient does vary with nitrate concentration. Synthetic nitrate and chloride solutions were prepared and the respective concentrations measured with nitrate and chloride electrodes. The solutions were then mixed, and nitrate and chloride measured again. From the initial nitrate concentration, the nominal concentration after dilution was calculated. This was compared with the final electrode measurement (after corrections for ionic strength differences). The final reading was higher because of electrode interference, and a percent error was calculated. The equation for percent error, derived from the modified Nernst relationship which includes the effect of interfering ions is as follows:

TABLE 2-V

SELECTIVITY COEFFICIENTS FOR VARIOUS INTERFERING IONS[10]

Ion	Selectivity Constant	Ion	Selectivity Constant
ClO_4^-	10^3	OAc^-	6×10^{-3}
I^-	20	CO_3^{2-}	6×10^{-3}
ClO_3^-	2	$S_2O_3^-$	6×10^{-3}
Br^-	0.9	SO_3^{2-}	6×10^{-3}
S^{2-}	0.57	F^-	9×10^{-4}
NO_2^-	6×10^{-2}	SO_4^{2-}	6×10^{-4}
CN^-	2×10^{-2}	$H_2PO_4^-$	3×10^{-4}
HCO_3^-	2×10^{-2}	PO_4^{3-}	3×10^{-4}
Cl^-	6×10^{-3}	HPO_4^{2-}	8×10^{-5}

$$\% \text{ error} = (100)\ (k_i)\left[\frac{A_i}{A_{NO_3^-}}\right] \qquad (2.8)$$

where:

k_i = selectivity constant for interfering ion i

A_i = activity of interfering ion i

$A_{NO_3^-}$ = actual nitrate activity

The value of k_i was calculated for various combinations of nitrate and chloride activities. Results are presented in Fig. 2-7 in terms of k_{Cl^-} vs. $A_{NO_3^-}$. It is apparent from Equation (2.8) that, for a given k_{Cl^-}, increasing values of $\frac{A_{Cl^-}}{A_{NO_3^-}}$ yield increasing percentage errors. However, Fig. 2-7 shows that at higher values of $A_{NO_3^-}$ where k_i is low, $\frac{A_{Cl^-}}{A_{NO_3^-}}$ will not cause as much error as at a lower nitrate concentration with the same chloride-nitrate ratio. Another interpretation is that at high nitrate concentrations, a relatively higher chloride concentration is required to cause the same percentage error as at a lower nitrate concentration. This relation of selectivity constant and nitrate concentration logically exists for other interfering ions as well, but has not been included in this study to date.

For purposes of comparison, Table 2-V shows that Cl^- and HCO_3^- are the two interfering ions which exist in large concentrations in tap water and have sufficiently large

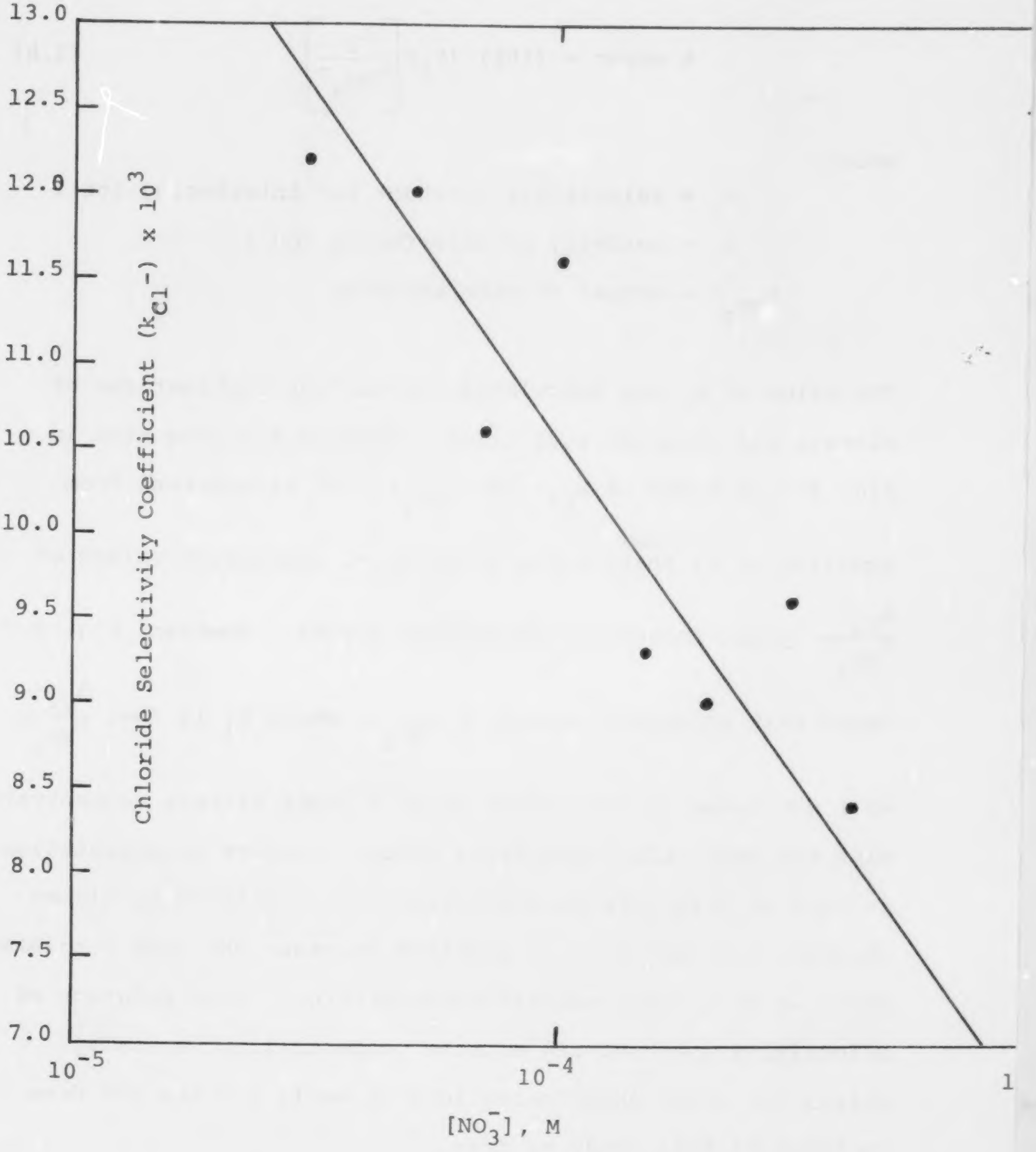


Figure 2-7. Nitrate concentration vs. chloride selectivity coefficient

selectivities to cause a problem with NO_3^- electrode measurements. For U.S. tap water, as reported by the USGS[3], the median chloride concentration is 5×10^{-4}M and the median nitrate concentration, 1×10^{-5}M. Using the appropriate selectivity constant from Fig. 2-7, the error which results is approximately 75%. Errors of similar magnitude exist for HCO_3^- interference. Errors caused by interference are not acceptable, and methods have been investigated for removing Cl^- and HCO_3^- from solution, or for correcting for their presence.

Using a cyclic approximation method, Equation (2.8) may be modified so that the interference of chloride can be corrected within 1% error. Since the actual nitrate activity in Equation (2.8) is not known, the measured nitrate activity is used to calculate a percent error, then corrected by that amount as a first approximation. This approximation is then used as the nitrate activity, and a second percent error is calculated. If this procedure is followed through three approximations, the third approximated nitrate activity equals the actual nitrate concentration within 1% error. By proper substitution, these three approximations can be combined to develop an equation relating measured nitrate activity to actual nitrate activity, if the interfering ion concentration and its selectivity coefficient are known. The equation is as follows:

$$A = \frac{M^4}{I^3k^3 + I^2k^2M + IkM^2 + M^3} \tag{2.9}$$

where:

A = actual nitrate activity
M = measured nitrate activity
I = interfering ion activity
k = selectivity coefficient

A similar equation can be developed to correct for both bicarbonate and chloride interference. For chloride interference, the value for k should be selected according to the approximate nitrate activity.

Electronic circuitry can be constructed to perform the necessary calculations automatically, using signals from nitrate and chloride electrodes as input, with a selectivity constant preset according to the approximate nitrate concentration.[13]

For HCO_3^- interference, alkalinity measurements provide an adequate bicarbonate concentration value to preset the circuitry or feed in continuously. Because of the high cost of the operational amplifiers, electronic compensation for interferences is not economically feasible if an alternate method with similar accuracy is available at lower cost.

One alternate approach is to remove interferences with separation techniques. Cl^- and HCO_3^- can be removed by addition of Ag^+ and Al^{3+} to form precipitates. However, unless these cations are added stoichiometrically (which is not feasible in samples of unknown composition) the excess cations cause erratic electrode response.[14] Paul and Carlson proposed the use of ion exchange resins in the Ag^+ and Al^{3+} forms to eliminate interference.[14] Orion modified this procedure and developed kits which can be used for batch determinations.[15] The feasibility of adapting this batch procedure to continuous measurements was considered in this study.

In the batch procedure, the resin is added to the sample and stirred for a few minutes. The mixture is then filtered and NO_3^- measured in the filtrate. In a continuous application, the resin could be contained in a column ahead of the measurement point. The residence time necessary to affect a desired reduction of Cl^- or HCO_3^- should be as short as possible to minimize the time between sampling and measurement. A short residence time can be accomplished by using a very small mesh resin to maximize resin surface area/unit volume. However, the pressure drop in a column containing very small, closely-packed resin beads is prohibitive. The reduction in chloride concentration using silver resins of various sizes was monitored with a chloride electrode in batch samples. The times necessary to achieve such reductions approximate residence times in a column, assuming equal resin-solution contact in both systems. Results are shown in Table 2-VI. The smallest resin (100-200 mesh) provided the best concentration reduction, but its dense packing caused a prohibitive pressure drop.

TABLE 2-VI

CHLORIDE CONCENTRATION REDUCTIONS WITH VARIOUS ION EXCHANGE RESINS

Resin Mesh Size	Chloride Concentration Reduction	Time, (minutes)
20-50	100-fold	20
50-100	10-fold	2
100-200	1000-fold	5

The necessary residence time for the 20-50 mesh resin resulted in a long delay in the sample-to-measurement time. The 50-100 mesh resin provided a satisfactory concentration reduction in a reasonable time. Similar results can be expected for bicarbonate-removing resin. These data indicate that two columns could be placed in series ahead of the nitrate measurement point to effect a significant reduction in chloride and bicarbonate concentrations and a proportionate decrease in the percentage error caused by these ions (see Equation 2.8).

A third method for reducing the error caused by interfering ions is to calibrate the electrode in nitrate standards prepared in water with composition similar to that of the sample. The chloride and bicarbonate composition of the water is determined by a time-average survey of the stream to be monitored. No data exist for the accuracy of this method. When the electrode is recalibrated each month after rejuvenation, calibration standards must be prepared in this synthetic water, but this consideration is minor when the improved accuracy is compared with the accuracy obtained when using the electrode with no correctional procedures.

A modification of this technique is the known addition calibration method, a technique which may be useful with other ion selective electrode measurements but is not applicable to nitrate determinations. The method consists of measuring the electrode potential in an unknown solution, adding a known volume and concentration of the ion to be measured, and measuring the new potential. Using the two potentials, the initial and final volumes, and the addition concentration, the original concentration can be determined. Two basic assumptions must be made: (1) that in the range of ion concentration being measured, the electrode response is Nernstian (linear) and the slope of the calibration is known, and (2) that interfering ions affect the addition to the same degree that they did the original sample. The second requirement is met in the case of complexing agents present in excess amounts which can complex the addition to the same degree as they did the original sample. This is not true for nitrate measurements, however, because relative chloride and bicarbonate interferences are less at the spiked NO_3^- level. Also, from 10^{-5}M to 10^{-4}M (0.62 to 6.2 mg/l, see Fig. 2-6), a common range of nitrate concentration, the calibration curve is not linear.

Considering the simplicity, cost and derived benefits of each of the above solutions for overcoming the loss of accuracy due to interfering ions, the third method - calibration of the electrode in synthetic water similar to the sample - is recommended. Even though only rough estimates of Cl^- and HCO_3^- concentrations are made in preparing the synthetic water, the accuracy is improved significantly.

Accuracy and Precision

The reported accuracy of the electrode is in the range of 1 - 5% in pure solutions of nitrate.[11,12] In this study, electrode determinations were compared with both brucine and phenoldisulfonic acid determinations, using synthetic solutions, and results were not significantly different. Variation is dependent upon the nitrate concentration itself. Because the electrode signal varies logarithmically with concentration, small changes in concentration at high levels cause little or no change in electrode potential. Thus, the electrode is more accurate at lower concentrations which show a linear Nernstian response.

In pure nitrate solutions, the accuracy of the electrode is excellent; and, in mixed solutions where concentrations of the interfering ions are known, correction for these interferences and for errors due to changes in ionic strength result in similar accuracy. For any batch, grab sample, or laboratory situation, measurements made with the nitrate electrode were shown to equal the accuracy of wet chemical techniques. It is only in monitoring applications, where corrections for interfering ions cannot be made continuously, that problems with accuracy, which require solutions as described in "*Selectivity*", may exist.

The precision of the electrode is generally satisfactory. This work and that of Potterton and Shults[11] show a reproducibility of electrode response in identical solutions of approximately 0 - 3%. Reproducibility error increased with the amount of time between the two readings resulting from deterioration and contamination of the liquid ion exchanger. Reproducibility becomes progressively worse and the electrode must be rejuvenated.

Long Term Stability

Various lengths of time have been proposed for the life of the electrode. To rejuvenate the electrode, the body must be disassembled, old solutions washed out, new reference and liquid ion exchanger solutions added, and the body reassembled. In the original instruction manual,[10] Orion reported the period between rejuvenations to be 30 days or more; but in the second edition, extended it to "several months".[10] Potterton and Shults report a life of three weeks,[11] and this study shows a life of approximately one month. Reassembly of the electrode causes not only a shift in relative position of the calibration curve, but a change in the slope of the linear portion.

In working with this electrode system, yellow-orange deposits were observed on the outside surface of the electrode membrane and on the bottom cap. These deposits are viscous substances, apparently liquid ion exchanger which has diffused out through the membrane and gelled. They may be partially responsible for shortening the life of the electrode.

Data on electrode life were obtained in batch systems with storage in aqueous solutions. Electrode life and the action of these deposits are now being studied in a flow through system.

2.323 Secondary Electrode Characteristics

Ionic Strength

Errors which result from changes in ionic strength, are described in Section 2.12, "Theory". Correction for these errors is possible with electronic circuitry. Fig. 2-1 has been redrawn on linear coordinates in Fig. 2-8, and the curve approximated by a series of straight lines which differ from the original curve by a maximum of 1.0%. Equations for these four lines are shown in Table 2-VII. It is possible to build circuitry which, upon receiving an appropriate signal from a conductivity bridge, will calculate γ and adjust the nitrate signal accordingly.

It is also possible to calibrate the electrode in water of ionic strength similar to that of the sample to be measured. Because ionic strength is a composite type of parameter, it does not change significantly over short periods of time, and relatively large changes do not seriously affect the nitrate activity coefficient. Therefore, unless the ionic strength of the water to be monitored is known to change significantly, this correction technique is recommended over the more complicated and costly electronic method. However, since almost all common anions interfere to some extent, a supporting electrolyte should

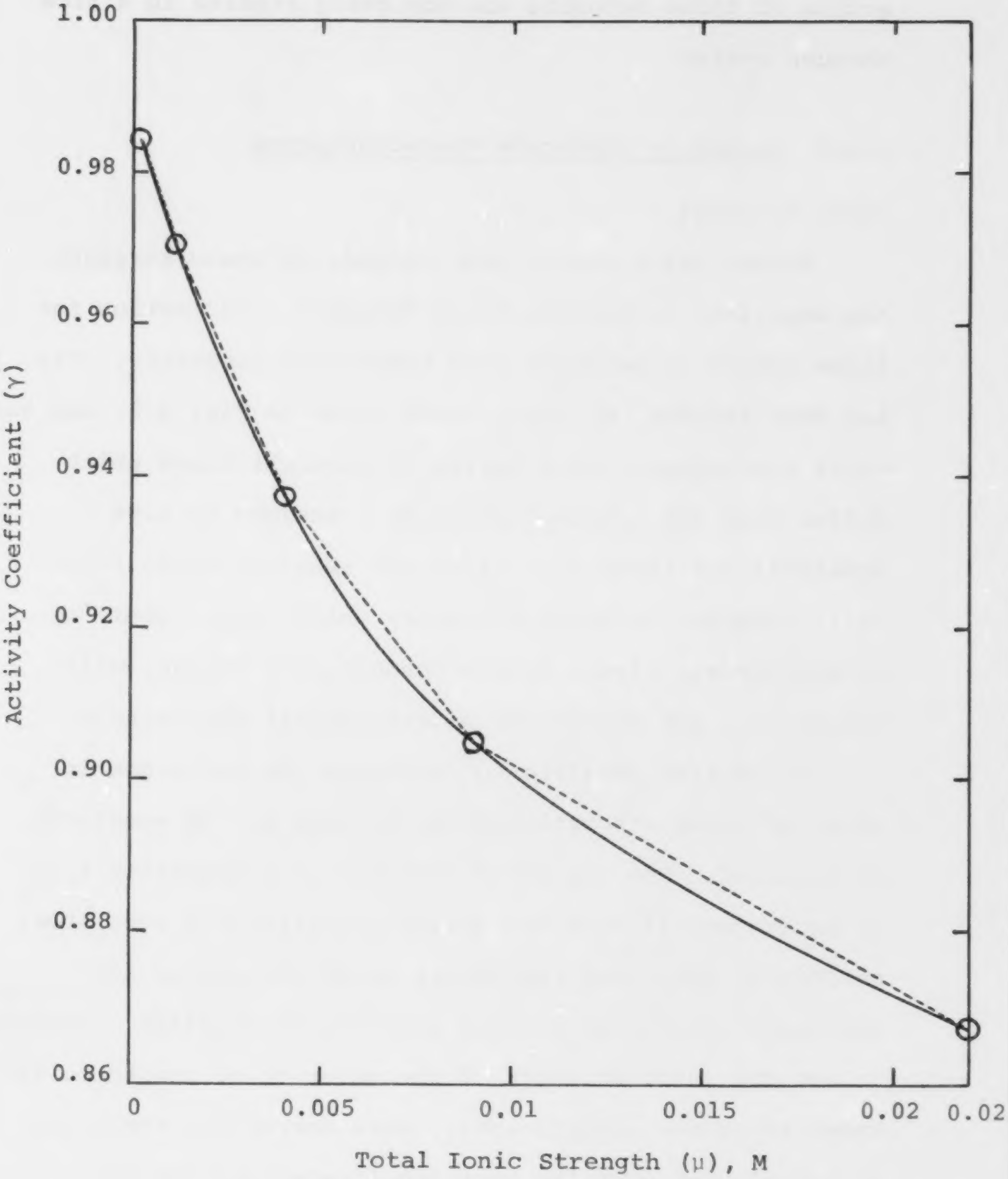


Figure 2-8. Total ionic strength vs. activity coefficient

Approximation of Fig. 2-1 (on linear coordinates) by four straight lines

TABLE 2-VII

EQUATIONS RELATING IONIC STRENGTH AND NITRATE ACTIVITY COEFFICIENT

Range of Ionic Strength	Equation for γ
$\mu = 0.0002M$ to $0.00115M$	$\gamma = \frac{0.04155 - \mu}{0.0432}$
$\mu = 0.00115M$ to $0.004M$	$\gamma = \frac{0.0954 - \mu}{0.0981}$
$\mu = 0.004M$ to $0.009M$	$\gamma = \frac{0.183 - \mu}{0.1921}$
$\mu = 0.009M$ to $0.022M$	$\gamma = \frac{0.252 - \mu}{0.2681}$

be chosen that has a very low selectivity coefficient, and correction should be made for the interference error introduced, before the calibration curve is constructed. Combining this technique with that recommended under "*Selectivity*" for accounting for chloride and bicarbonate interference could result in using Cl^- and HCO_3^- salts as the supporting electrolyte, depending on the interference and ionic strength levels encountered.

Temperature

The Nernst factor is temperature dependent; thus, if the electrode is calibrated at a temperature other than that of the test solution, the measured potential does not represent the true nitrate activity. Orion[10] states that a ±2°C. temperature variation from the calibration temperature is insignificant in its effect on accuracy.

If the sample temperature and the calibration temperature are similar but the internal electrode standard temperature is different from previous immersion in a sample of different temperature, there is a time delay required for the internal standard temperature to equilibrate. In continuous monitoring applications, temperature effects can be overcome by heating or cooling the sample to calibration temperature before measurements are made. This technique is applicable to monitoring with any ion selective electrode.

pH

The manufacturer's recommended range of pH in which the electrode may be used is 2-12.[10] At the upper limit, the OH^- concentration is sufficiently high to be sensed by the electrode. At the lower limit, the electrode body and membrane junction assembly are attacked and permanent deterioration results.

2.324 Feasibility for Potable Water Monitoring Applications

The nitrate electrode is applicable to the continuous analysis of water supplies. It is quite accurate (1-5% error) in pure nitrate solutions, and the lower limit of sensitivity of about 0.6 mg/l is sufficient to provide meaningful electrode response at any nitrate concentration which is thought to be significant in U.S. tap waters. However, the liquid ion exchanger deteriorates sufficiently to produce significant errors after approximately one month, and the electrode must be rejuvenated and recalibrated at that time. Within the one month period, precision of the electrode is within 3%. Changes in ionic strength affect electrode response but these effects are known, and the resulting error can be corrected, either manually or electronically, to provide accurate measurement. If the temperature is maintained within ±2°C., and the pH between 2 and 12, no problems are associated.

When the electrode is used in monitoring situations, continuous correction for - or elimination of Cl^- and HCO_3^- must be considered. This can be accomplished by calibrating in water similar to the sample stream.

2.33 CHLORIDE

2.331 General

The maximum permissible level for chloride in drinking water was established as a result of its taste properties.[16] With the development of ion selective electrodes, chloride levels in distribution systems can be measured continuously with accuracy equivalent to that available with standard wet chemical techniques.[5] In this project, three models of the chloride electrode were evaluated with respect to their adaptability to potable water monitoring. The liquid junction membrane electrode, Orion 92-17, was quickly rejected because of its frequent rejuvenation and recalibration requirements. The solid state membrane electrode, Orion 94-17A, was selected in preference to the larger solid state electrode, Orion 94-17, as a result of its consistently faster response time and better Nernstian relationship (∿ 2% compared with 10% error in slope). Performance characteristics of the Model 94-17A are discussed in the following section of this report.

2.332 Primary Electrode Characteristics

Sensitivity

The range of chloride concentrations found in U.S. tap water is approximately 2×10^{-4}M to 2×10^{-2}M.[3] The manufacturer's stated range of sensitivity for this electrode is 5×10^{-5}M to 1M.[2] This study indicates that the lower range of sensitivity can be extended to 1×10^{-5}M without serious error (Fig. 2-9), although response is not Nernstian at the lower levels. In either case, the upper and lower chloride concentrations found in potable water are well within the electrode's range of concentration sensitivity.

Selectivity

The chloride electrode is extremely selective for chloride over other ions. The manufacturer lists some common anions with a constant that is the maximum allowable ratio of interfering ion concentration to chloride ion concentration, before an error of 1% is observed.[2] In potable water, the only interfering ion with a sufficiently low ratio and sufficiently high concentration to be an important interference is hydroxide ion. The maximum allowable OH^-:Cl^- ratio is 80. At a chloride concentration of 2×10^{-4}M, the lowest found in U.S. tap water,[3] the maximum allowable pOH is 1.8, or maximum allowable pH, 12.2. No U.S. tap water is expected to have a pH higher than 12.2, so no problems of interference by hydroxide, or any other ion, exist.

Accuracy and Precision

In pure chloride solutions, the accuracy of the electrode, when compared with the mercuric nitrate method,[5] is ± 1%. This applies only to laboratory situations where the temperature and ionic strength are either controlled or corrected. Reproducibility measurements over a period

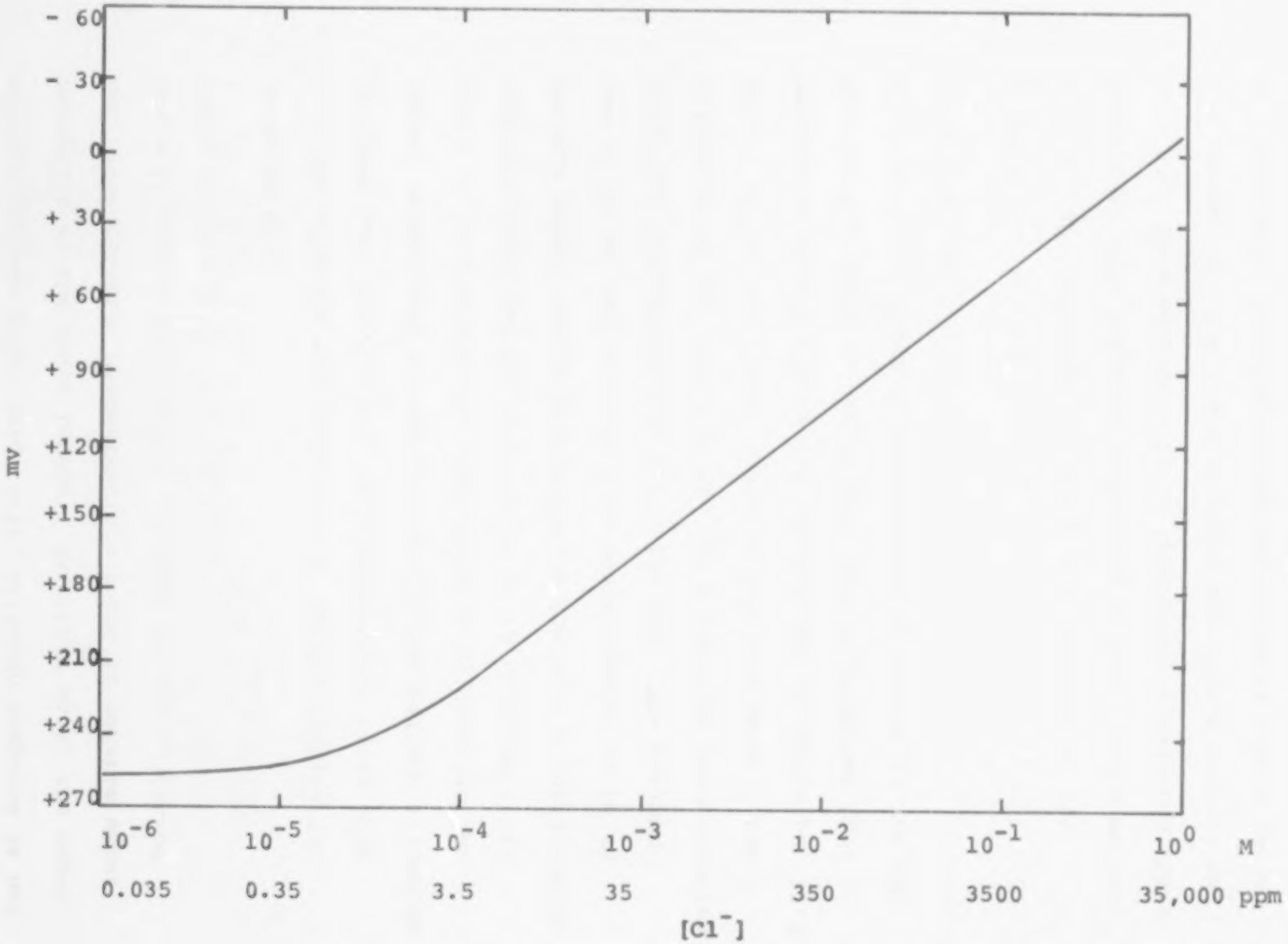


Figure 2-9. Chloride calibration curve

of several days indicate that readings do drift slightly but not in a constant direction, and never more than ± 1%, in terms of concentration.

Long Term Stability

Solid state electrodes are unusually stable and require no periodic rejuvenation. The stable life of the chloride electrode can be reported in terms of months, and a routine monthly calibration check is the only maintenance requirement. Drift and non-reproducibility are more likely to be caused by the reference electrode than by the chloride electrode.

2.333 Secondary Electrode Characteristics

Ionic Strength

Errors which result from changes in ionic strength are significant. Since Cl^- and NO_3^- are both monovalent anions, the relation of total ionic strength to activity coefficient (Fig. 2-1) applies to both. Consequently, the linear approximation of this relation (Fig. 2-8) and the list of equations describing the approximations (Table 2-VII) are also applicable. Accordingly, the same type of electronic correction described for nitrate (Section 2.323) can be used for chloride. As with nitrate, however, if the ionic strength of the water to be measured does not change appreciably, calibration of the chloride electrode in water with ionic strength similar to that of the sample, using a non-interfering supporting electrolyte ($NaNO_3$, for example), is the method of choice.

Temperature

Variations in temperature affect both the calibration curve slope and the equilibrium temperature of the internal reference solution. Therefore, in monitoring applications, it is desirable to maintain the sample at the calibration temperature by controlled heating or cooling up-stream of the measurement point.

pH

Hydrogen ion attack on the electrode at low pH levels results in permanent deterioration of the electrode body and membrane assembly. OH^- interferes with electrode response at high pH levels (see *Selectivity*). The recommended pH range is 2-12.[2]

2.334 Feasibility for Potable Water Monitoring Applications

In general, solid state selective ion electrodes have proved to be exceptionally accurate, easily maintained and operated analytical tools. The chloride electrode is no exception. Its range of sensitivity easily includes the range of chloride concentrations found in U.S. tap waters: accuracy and precision are within ± 1%; stable life is at least a year with routine monthly calibration checks; the electrode is not subject to interference by other ions: the effect of changes in ionic strength is known and can be corrected electronically or manually. If pH and temperature are controlled, effects of changes in these parameters are eliminated. The chloride electrode appears to be useful for potable water quality monitoring applications.

2.34 FLUORIDE

In lieu of describing the fluoride ion selective electrode in the format adopted for other electrode evaluations, the complete text of a paper recently submitted for publication is included in this report. References follow the paper and are not included in the general reference section of the report.

ELECTROCHEMICAL CHARACTERIZATION
OF FLUORIDES IN DRINKING WATERS

1) Nabih P. Kelada, 2) Nina I. McClelland and 3) K. H. Mancy

1) Research Associate, National Sanitation Foundation, Ann Arbor, Michigan

2) Program Director, National Sanitation Foundation, Ann Arbor, Michigan

3) Professor, School of Public Health, University of Michigan, Ann Arbor, Michigan

Abstract

Procedures for measuring free, complexed and total fluorides using potentiometric membrane electrodes have been developed. The significance of determining the type and distribution of fluorides in drinking waters and the analytical feasibility of this technique is discussed.

Public health aspects and the safety of fluoridation are well documented.[1,2] However, increasing public acceptance of fluoridation for dental caries prevention indicates that the chemistry of fluorides in water supplies be better defined. Little or no attention has been given to the degree and types of chemical transformations of fluorides from the time they are added in the water treatment plant to the time they are consumed from the water distribution system.

Fluorides are added in water supplies as sodium fluosilicate (Na_2SiF_6), fluosilicic acid (H_2SiF_6), or sodium fluoride (NaF), each of which dissociates to release free fluoride ions (F^-). It has generally been assumed that fluorides are acquired by the consumer in the same form they are added; i.e., fluoride ions, and that fluorides added routinely during the treatment of drinking waters are not different from those present in certain natural waters.

The validity of these assumptions is doubtful. It is likely that fluorides in most chemically treated water supplies are complexed to a certain degree with aluminum and ferric ions, commonly added as coagulants in the treatment process. Accordingly, drinking waters delivered to the consumer may contain variable quantities of free and complexed fluorides depending on the presence of complexing metals and the pH of the water.

A literature review indicates that free F^- [3,4,5,6], not complexed fluorides[7,8], react with dental enamel to prevent and control dental caries, as shown in the following reactions:

$$\mathrm{Ca_{10}(PO_4)_6(OH)_2 + 20\ F^- + 8H^+ \rightarrow 10\ CaF_2 + 6HPO_4{}^{2-} + 2H_2O} \qquad (1)$$

Hydroxylapatite (Dental enamel) → Calcium fluoride

or

$$\mathrm{Ca_{10}(PO_4)_6(OH)_2 + 2\ F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2\ OH^-} \qquad (2)$$

Hydroxylapatite → Fluorapatite

Reaction (1) is generally favored in the presence of high concentrations of F^- such as those found in dentifrices. Reaction (2) is generally favored in the presence of low levels of F^- such as those found in fluoridated water supplies.[9]

There is a need for developing reliable analytical procedures capable of differentiating between free, complexed and total fluorides in water supplies. Measurement of the forms of fluoride, rather than total fluorides, per se, may help in determining the effectiveness of fluoridation practice.

It is essential that the form of fluorides be determined by simple analytical procedure so that the method can easily be used on a routine basis in water treatment plants and in surveying water quality in the distribution system. Needless to say, if the procedure is simple enough, it may be amenable to automation for use in continuous monitoring applications.

This paper describes procedures in which potentiometric membrane electrode systems, commonly known as selective ion electrodes, are used for the measurement of free, complexed and total fluorides in drinking waters. The effects of pH and interferences are discussed in detail. The applicability and limitations of this procedure for laboratory analysis and continuous monitoring applications are presented.

Theory

Various applications for the recently developed lanthanum fluoride selective ion electrode have been discussed in the literature.[10,11,12,13,14,15] Theoretical aspects of such electrode systems have been discussed in detail.[16,17,18,19,20] The electrode system, basically a potentiometric membrane electrode, may be described schematically as follows:

Internal Reference Electrode	Internal Reference Solution $[XF]_r$	Membrane	External Solution $[YF]_t$	External Reference Electrode
Ag/AgCl	$AgCl_{(s)}$, Cl^-, F^-	LaF_3	Test Solution	Standard Calomel Electrode (S. C.E.)

Vertical lines represent boundaries or liquid junctions between components of the cell. Measurements are based on the Nernstian relationship, stated as follows:

$$E_m = E_o - \frac{RT}{zF} \ln \left[a_{F^-} + \sum_i K a_i^{a_i/a_{F^-}} \right] \tag{3}$$

where: E_m = measured potential

E_o = a constant equal to the sum of the potentials at the Ag/AgCl electrode, the standard calomel electrode, the liquid junction potential between the test solution and the reference electrode, and the potential across the membrane when the F^- activity in the test solution is unity

R = gas constant

T = absolute temperature

F = the Faraday

z = number of electrons involved in the electrode reaction

a_{F^-} = activity of F^-

a_i = activity of i^{th} interfering ion, and

K = selectivity coefficient of interfering ion with respect to F^-

Activity (a) is related to concentration (c) as shown in the following empirical expression:

$$a = \gamma c \tag{4}$$

where: γ = the activity coefficient

At 25°C. the slope of the line described by Equation (3) will be approximately 60 mv. In practice, measurements are usually based on the use of calibration curves. Because the electrode is sensitive to the activity of free fluoride ions, it is important to account for the effect of changes in total ionic strength of the test solution on the activity coefficient. Errors due to variations in the ionic strength of drinking waters in the U.S.A.[21] are estimated to be approximately 10%.

Interferences

It is generally accepted that interferences with selective ion electrode measurements are caused by potential determining ions other than the ion of interest. In the case of the fluoride electrode, the only significant interfering ions are hydroxide ions (OH^-).[16,18] Thus, measurements at high pH values will be subjected to OH^- interferences.[16,18,22] This effect is noticeable when the level of hydroxide ions is greater than one tenth the level of fluoride ions present.[16,18]

Other anions commonly found in drinking water are Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, and PO_4^{3-}; but these ions do not interfere even when they are present in excess of one thousand times the level of F^-.[16,20,23,24,25]

Interferences due to hydroxide ions should be differentiated from the complexing effect of certain cations which may be present in the test solutions, e.g., H^+, Al^{3+}, Fe^{3+}, etc.[16,23] Under proper physiochemical conditions, these cations will form fluorocomplexes which cannot be sensed by the membrane electrode. Because the prime objective of this investigation is the characterization of free versus complexed fluorides, it is not appropriate to consider that the cation complexing effect constitutes interference with the electrode measurement.

Experimental

An Orion Model 94-09 selective ion electrode was used in these studies. Potential measurements versus saturated calomel electrode were made using an Orion digital potentiometer, Model 801. Polyethylene containers were used to minimize the loss of fluoride by adsorption on glassware.

In studying the effect of pH, a stock solution of sodium fluoride was prepared from which suitable dilutions were made. pH was varied by addition of strong acids and bases, and the ionic strength was maintained at 0.5M by addition of appropriate volumes of concentrated sodium nitrate ($NaNO_3$) solution. Potentials were measured after equilibrium was established; at low fluoride and high pH levels, 10-15 minutes were required to reach equilibrium.

Complexometric titration techniques were used to characterize aluminum-fluoride complexes. pH was controlled by an acetate buffer. Ethanol was used to suppress the solubility of the aluminum-fluoride complex.

To determine total fluorides, a masking agent is needed which complexes Al^{3+} more strongly than does F^-, and thereby liberates bound F^-. The efficiencies of a number of masking agents were compared. These included: (1) EDTA (disodium salt of ethylenediaminetetraacetic acid), (2) CDTA (cyclohexanediaminetetraacetic acid), (3) oxalate, and (4) citrate. In this study, a Corning digital electrometer, Model 101, was used in the activity mode. Calibration was made so that the upper limit read "100" for $5 \times 10^{-5}M$ F^- and the lower limit, "20" for 10^{-5}M F^-. This made it possible to read percent recovery of fluoride in the test solutions directly.

Results and Discussion

Before a procedure could be developed for measuring free, complexed and total fluorides using selective ion electrodes, it was necessary to investigate the effects of pH on the electrode sensitivity and fluoride complex formation.

Effect of pH

Typical results of the pH effect on the fluoride electrode are shown in Fig. 1. The interference effect of OH^- is predominant at high pH values where the curves show a non-linear relationship and shift toward more negative potentials. Because fluoride and hydroxide ions have similar charges and ionic radii[16], the electrode senses both in a similar manner but to varying degrees, and a false increase in F^- activity may occur.

The effect of complex formation is shown at low pH values. Hydrogen ions combine with fluoride ions to form hydrogen fluoride (HF) and bifluoride ion (HF_2^-) neither of which are sensed by the electrode.[26,27]

It has been recommended that the applicable pH range for using the fluoride electrode in drinking waters is from pH 5 to 8.[16,18] However, data obtained in this study indicate that the optimum pH range for proper use of the fluoride electrode is more restricted, as shown in Fig. 1. At 10^{-6}M F^-, the optimum range is from 5.0 to 5.4. A pH value of 5.2 is therefore recommended for electrode measurement of fluorides in water supplies.

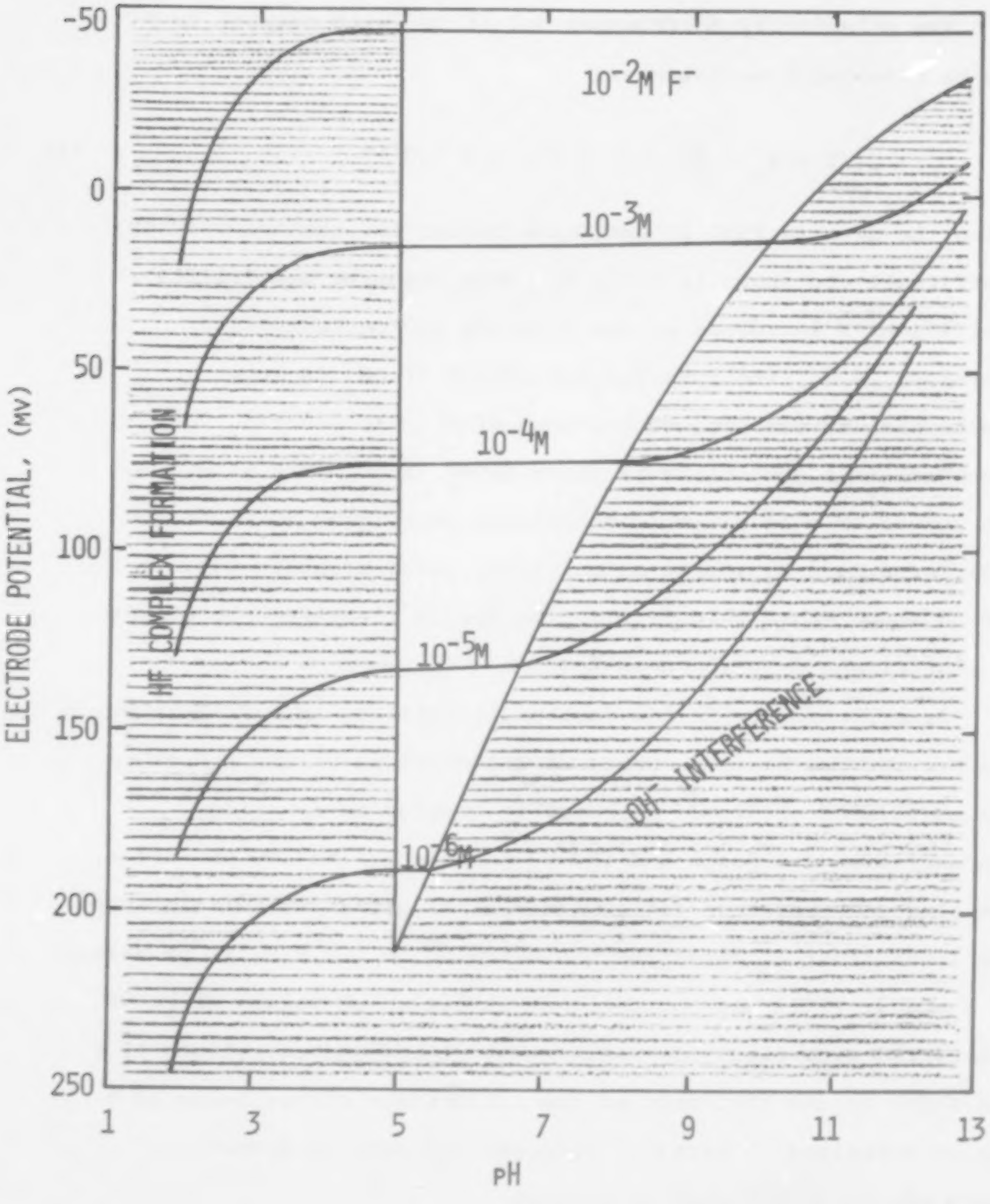


FIGURE 1

EFFECT OF pH ON FLUORIDE ION SELECTIVE ELECTRODE MEASUREMENT

The selectivity coefficient (K) of OH^- with respect to F^- can be calculated as follows:

$$E = E_o - \frac{RT}{F} \ln \left[(F^-) + K\,(OH^-) \right] \qquad (5)$$

Using the data in Fig. 1, estimated values for the selectivity coefficient are shown in Table I. Note that the selectivity coefficient K increases as the fluoride ion concentration decreases, i.e., the interference effect of OH^- is more predominant at lower concentrations of F^-. At fluoride ion concentrations comparable to those found in drinking waters, the values of selectivity coefficients were found to be on the order of 0.70. By simple calculation, using Equation (5), it can be shown that at $10^{-6}M$ fluoride the OH^- interference effect is significant only above pH 5.4.

Interference by OH^- is further illustrated in Fig. 2 in which a series of calibration curves at different pH values are shown. The non-linear electrode response is greater as fluoride concentration decreases and the pH increases. At low pH values, the electrode response followed a typical Nernstian relationship. The lower limit of detection was extended to $10^{-6}M\ F^-$ at pH values of 2 and 3. This was not the case at higher pH values where OH^- interfered with electrode measurement at low concentrations of F^-. The shift in the intercept of the calibration curves below pH 5 can be explained in terms of hydrogen ion complex formation, which may be illustrated as follows:

$$[F^-]\ [H^+] = K_1\ [HF] \qquad pK_1 = 2.9 \qquad (6)$$

$$[HF]\ [F^-] = K_2\ [HF_2^-] \qquad pK_2 = 0.77 \qquad (7)$$

TABLE I

OH^- SELECTIVITY COEFFICIENTS (K)

F^- Concentration	K
$10^{-6}M - 10^{-4}M$	0.70
$10^{-4}M - 10^{-3}M$	0.07
$10^{-3}M - 10^{-2}M$	0.05

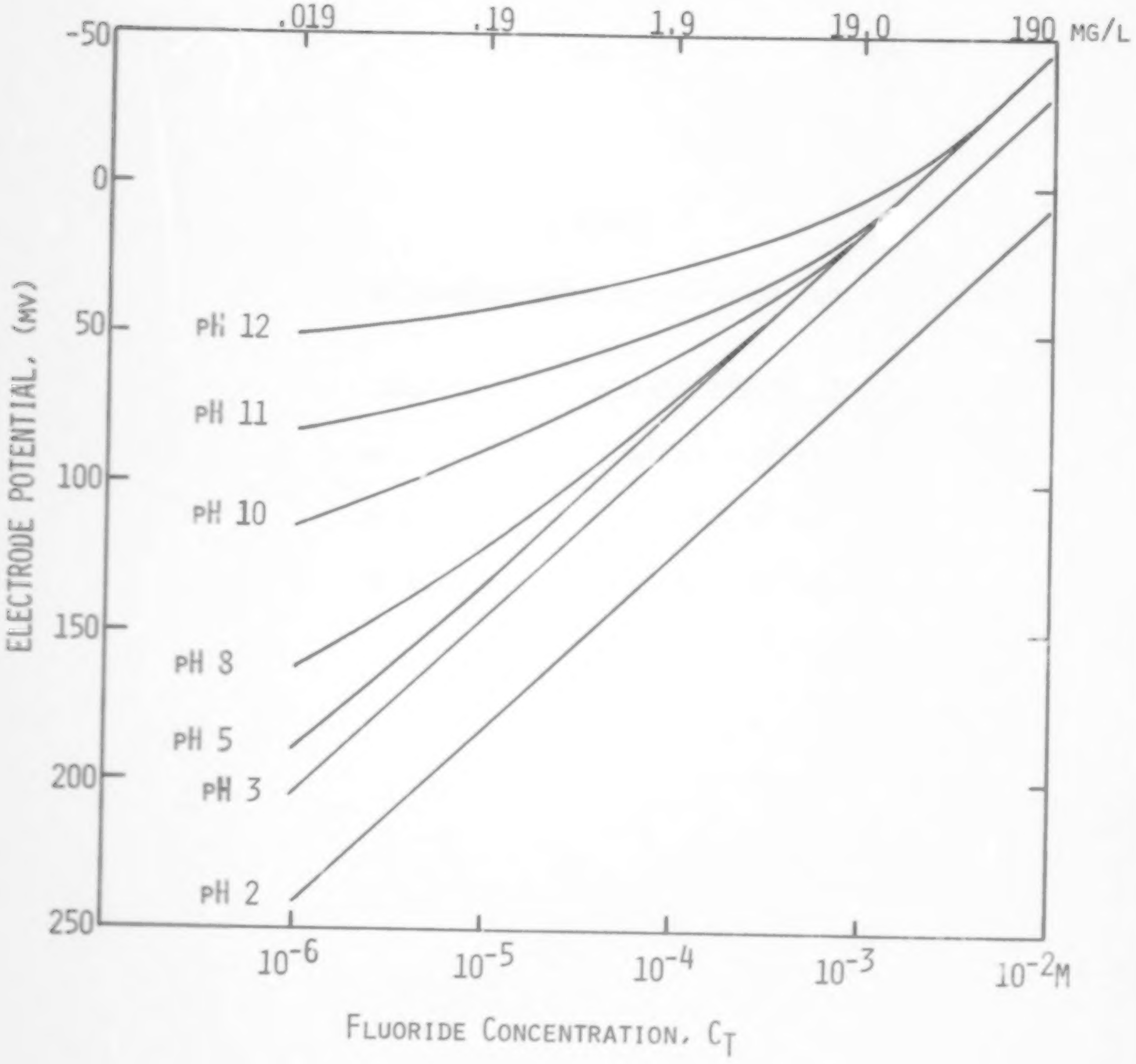


FIGURE 2

CALIBRATION CURVES AT DIFFERENT LEVELS OF pH where K_1 and K_2 are dissociation constants.[26]

The total concentration C_T will be:

$$C_T = 2\,[HF_2^-] + [HF] + [F^-] \qquad (8)$$

In solutions more dilute than 0.05M, it is possible to neglect $[HF_2^-]$[28] and Equation (8) may be approximated to give:

$$C_T = [HF] + [F^-] \qquad (9)$$

From Equations (6) and (9), it follows that:

$$[F^-] = C_T \frac{K_1}{K_1 + [H^+]} \qquad (10)$$

Substituting Equation (10) into the Nernst relationship and rearranging gives:

$$E = E_o - \frac{RT}{F} \ln \frac{K_1}{K_1 + [H^+]} - \frac{RT}{F} \ln C_T \qquad (11)$$

where the term $\frac{RT}{F} \ln \frac{K_1}{K_1 + [H^+]}$, called the shift term, is a constant for a given pH and temperature, and represents a shift in the potential at $C_T = 10^{-2}$M. At pH values above 5, $[H^+]$ is relatively small and the ratio $\frac{K_1}{K_1 + [H^+]}$ approaches unity, giving a value of zero for the shift term; i.e., no shift occurs, as shown in Fig. 2. At pH values below 5, $[H^+]$ is large, and the shift term is positive, representing shifts in the potential at $C_T = 10^{-2}$M which increase with decreasing pH.

A comparison between the calculated values of 0.059 log $\frac{K_1}{K_1 + [H^+]}$ and the experimentally determined values of the shift in the intercept at 25°C., shows good correlation, as illustrated in Table II.

From this discussion, it follows that, at constant pH, the effect of the H^+ complex formation is constant at all fluoride concentrations and exerts no effect on the slope of the calibration curve. Consequently, at any given pH, changes in the slope of a calibration curve within the sensitivity limits of the electrode are due to OH^- interference only. The family of curves shown in Fig. 3 shows the effect of pH on the sensitivity of the fluoride ion selective electrode.

Aluminum-fluoride Complex Formation

Another factor that should be accounted for in the characterization of fluorides in drinking water is aluminum-fluoride complex formation. Depending on the type and concentration of chemicals used in the water treatment process, aluminum may be found in drinking waters at concentration levels between 3.3 and 1500 micrograms per liter (μg/l).[21] Measurement of aluminum in tap water in Ann Arbor, Michigan over the period from March 1970 to February 1971 using emission spectroscopy showed variations in concentrations from less than 20 μg/l to 500 μg/l. Aluminum in drinking waters is considered significant because it forms a highly stable complex with F^- which may not be dissociated upon ingestion.

The aluminum-fluoride complex was characterized by means of a potentiometric titration technique, using the fluoride selective

TABLE II

SHIFT IN INTERCEPT OF CALIBRATION CURVES AT LOW pH VALUES

pH Range	Calculated	Experimental
2 - 3	36 mv	40 mv
3 - 5	14 mv	15 mv
2 - 5	50 mv	55 mv

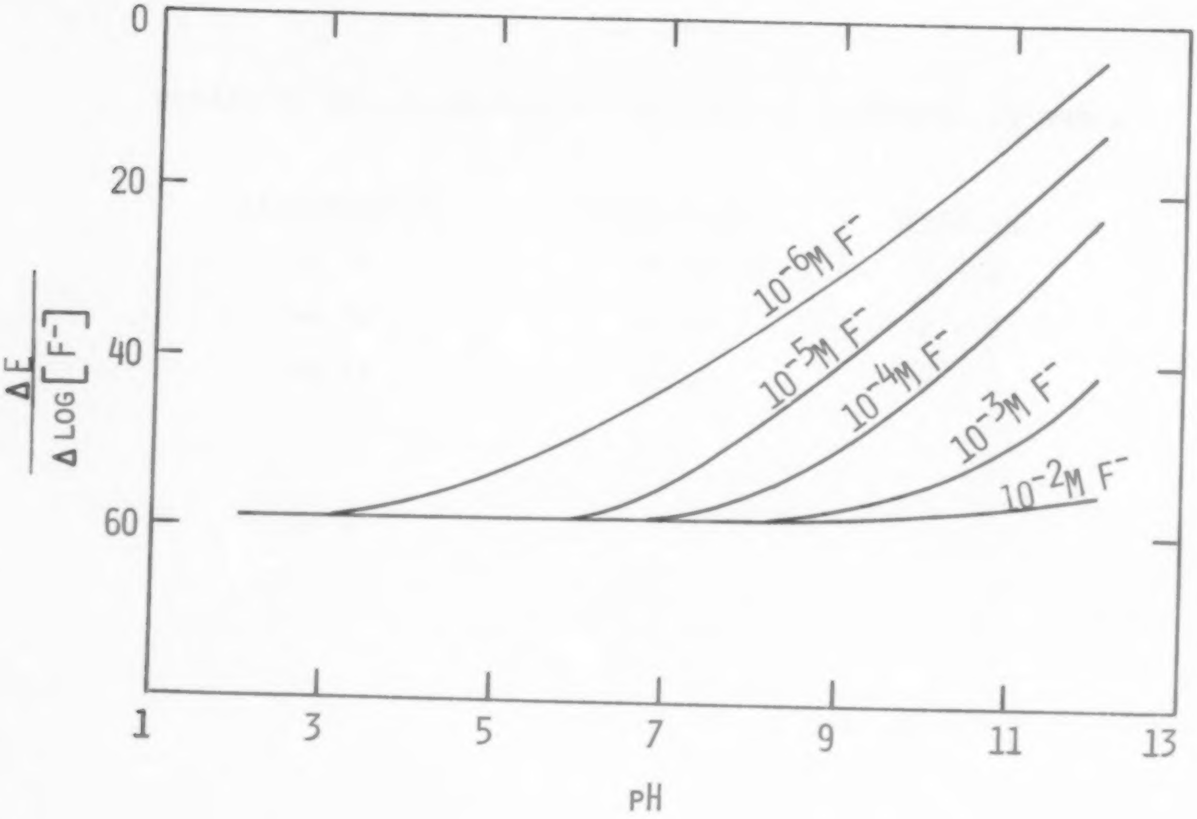


FIGURE 3

EFFECT OF pH ON FLUORIDE ION ELECTRODE SENSITIVITY ion electrode. Typical results, shown in Fig. 4, indicate that the complex formed is $(AlF_6)^{3-}$. This was determined by stoichiometric calculations of the complex coordination number, using the data presented in Fig. 4. The addition of acetate buffer to maintain an optimum pH of 5.2 improved end point detection considerably. Without pH control, the addition of Al^{3+} titrant lowered the pH of the test solution, resulting in further complexation of fluorides with hydrogen ions. Addition of ethanol to the test solution caused a marked improvement in the titration curve. This was attributed to suppression of the solubility of the aluminum fluoride complex.[12,29]

These titration data were used as diagnostic criteria for characterizing aluminum fluoride complex compounds in drinking waters.

Masking Agents

Masking agents, which form stable complexes with aluminum, are used to liberate the bound fluoride ions. This is a necessary step in the measurement of total fluoride by selective ion electrodes.

A number of masking agents have been proposed, e.g., citrate by Frant and Ross[17,18], CDTA by Harwood[23] and EDTA by Crosby et al.[30] This investigation was necessary to determine: a) the percent recovery of fluoride after the addition of the masking agent based on equilibrium measurement, and b) the rate at which this reaction takes place. Determination of the rate of liberation of fluorides by the addition of masking agents was made for automation and continuous monitoring purposes.

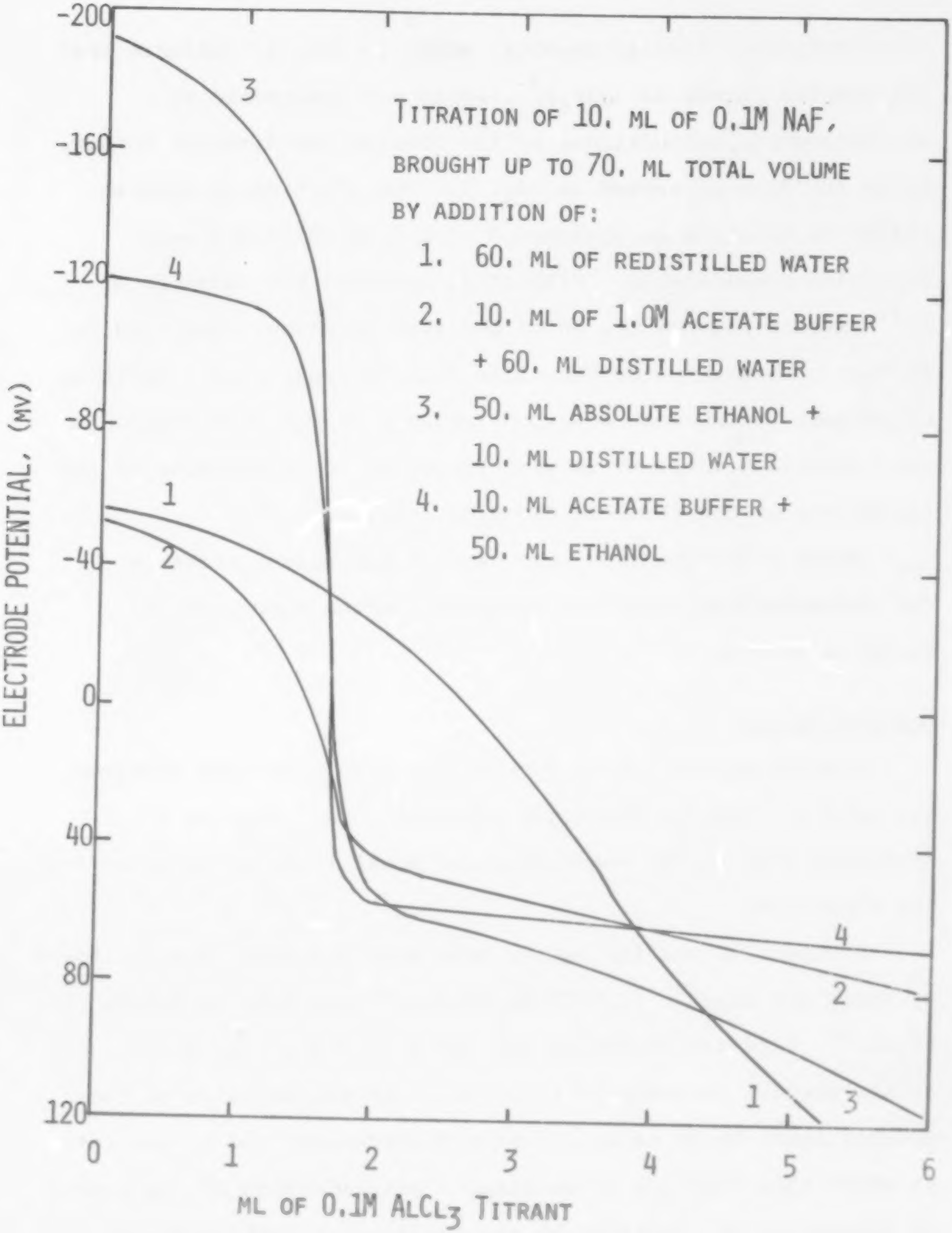


FIGURE 4

COMPLEXOMETRIC TITRATIONS OF FLUORIDE WITH ALUMINUM

Four different masking agents were evaluated: oxalate, citrate, EDTA and CDTA. The evaluation was based on comparing the effectiveness of corresponding equivalent weights of each. Results are shown in Table III. Increasing amounts of aluminum were added to standard solutions containing a constant concentration of fluoride ions, 5×10^{-5}M or approximately 1.0 mg F^-/l, to form the aluminum hexafluoride. When complexation was complete, the various masking agents were added in different concentrations, and the percentage recovery of fluoride was calculated. This was done in the presence of 1.0M acetate buffer (pH = 5.2) with constant ionic strength (1.0M of $NaNO_3$). Equilibrium values of percent recovery for three different concentrations of each masking agent are shown in Table III. In the presence of acetate buffer alone, a certain amount of recovery was obtained. Addition of EDTA and oxalate did not provide high recoveries. The best fluoride recovery was achieved by 60.0 milliequivalents per liter (meq/l) of citrate (Fig. 5 and Table III). At 6.0 meq/l of each masking agent, CDTA provided the highest percent recovery, but at higher concentrations, citrate proved to be the most efficient. This is in contrast to CDTA with which there was no improvement in fluoride recovery at higher concentrations.

Iron-fluoride Complex Formation

Iron is frequently found at higher concentrations than aluminum in drinking waters. This is reported to be in the range of 2 to 1700 μg/l.[21]

TABLE III

ALUMINUM COMPLEXING EFFECT AND FLUORIDE RECOVERY BY DIFFERENT MASKING AGENTS

		% Recovery of Fluoride							
Aluminum Conc.	meq/l	0.0	0.006	0.012	0.024	0.06	0.12	0.6	1.2
	mg/l	0.0	0.054	0.108	0.216	0.54	1.08	5.4	10.8
Acetate Buffer		100	94	90	82	62	48	15	10
	meq/l								
EDTA	6.	101	98	94	88	81	69	24	15
	30.	100	97	92	86	80	69	25	16
	60.	100	97	90	85	79	68	27	15
Oxalate	6.	100	99	96	94	89	85	54	32
	30.	102	100	97	96	93	91	82	67
CDTA	6.	102	101	99	97	95	92	86	73
	30.	101	100	97	95	91	87	85	73
	60.	100	100	97	94	89	85	82	73
Citrate	6.	101	100	100	99	95	92	67	52
	30.	101	100	100	100	100	99	89	83
	60.	102	101	101	100	101	100	95	91

(Masking agents added to standard solutions containing 5 x 10^{-5}M fluoride, and variable aluminum concentration)

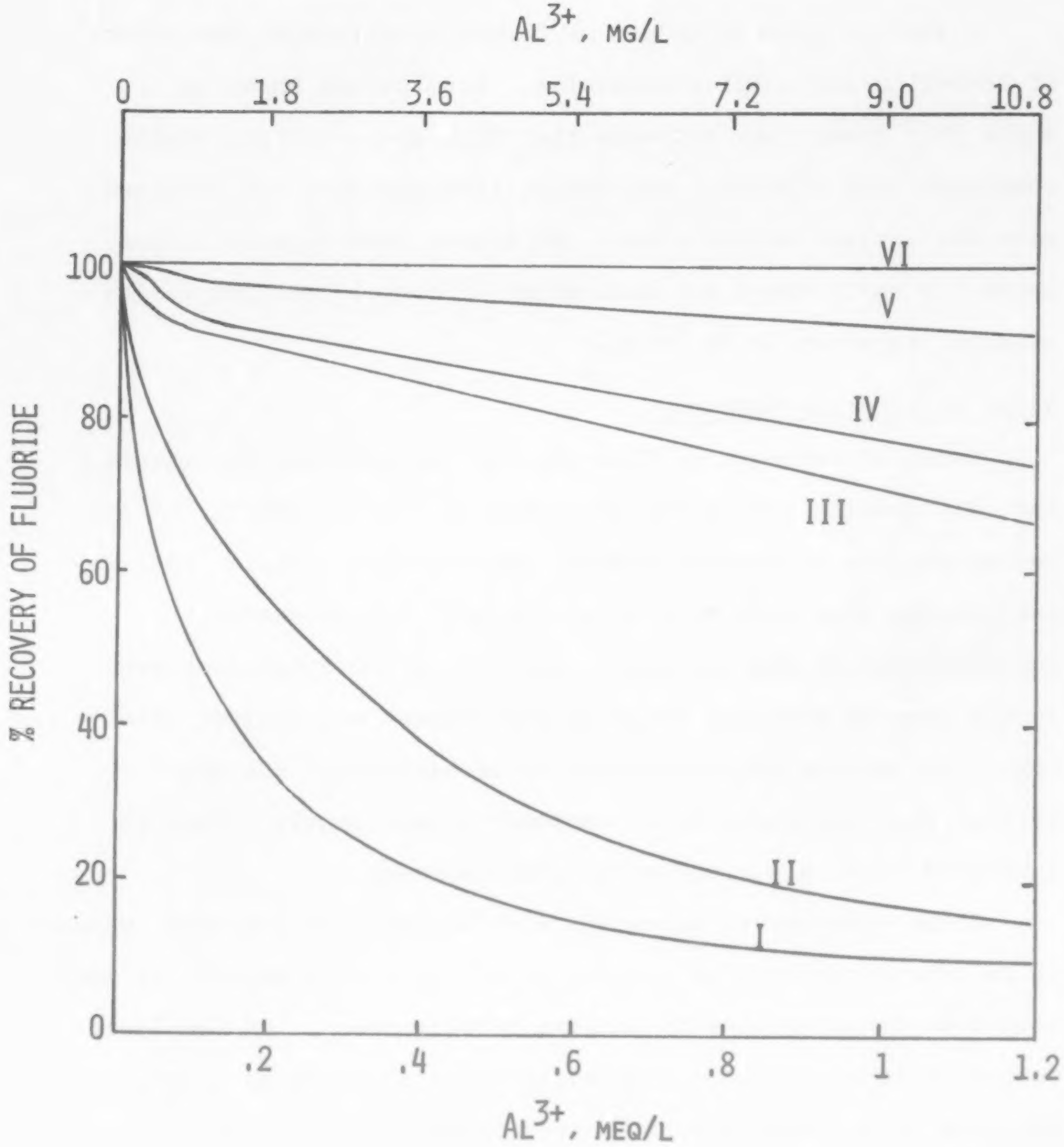


FIGURE 5

ALUMINUM COMPLEXING EFFECT AND FLUORIDE RECOVERY BY DIFFERENT MASKING AGENTS

I.	Acetate Buffer	IV.	CDTA, 60 meq/l
II.	EDTA, 60 meq/l	V.	Citrate, 60 meq/l
III.	Oxalate, 30 meq/l	VI.	Citrate, 200 meq/l

A similar experiment was performed to determine the effect of iron-fluoride complex formation. Results are shown in Table IV. These data indicate that iron does not form stable complexes with fluoride, and almost 100% recovery was obtained with the acetate buffer alone. At higher iron concentrations, above 2.0 mg/l, there was indication of competitive complexing effects, as shown in Table IV.

Rates of Fluoride Recovery

Rates of recovery of fluorides by the addition of citrate and CDTA masking agents are presented in Figs. 6 and 7. At low concentrations of masking agents, the rates of fluoride recovery were higher with CDTA than with citrate. On increasing the concentration of masking agent, the rate of reaction increased in the case of citrate, while no improvement was noticed with CDTA. Increasing the concentration of citrate to 600 meq/l (0.2 M) improved the rate of recovery significantly. This was estimated to be 6.5 minutes for 100% recovery.

These experiments were done with 0.5 mg/l of aluminum, which is an exceptionally high value. At 0.1 mg/l of aluminum, it took less than three minutes to achieve 100% recovery. At the lower concentrations of aluminum normally found in drinking water, the rate of recovery should be even faster.

Measurement Procedures

Free Fluorides

Selective ion electrode measurement of free fluorides is based on adding an appropriate quantity of acetate buffer to control the pH at 5.2. It is essential in this measurement that

TABLE IV

IRON EFFECT AND FLUORIDE RECOVERY BY MASKING AGENTS

		% Recovery of Fluoride								
Iron	meq/l	0.0	0.006	0.012	0.024	0.06	0.12	0.6	1.2	2.4
Conc.	mg/l	0.0	0.11	0.22	0.45	1.12	2.23	11.17	22.34	44.68
Acetate Buffer		100	101	101	100	100	99	98	95	84
CDTA	meq/l 30.	100	100	100	100	100	100	100	99	98
Citrate	6.	100	100	100	100	100	100	100	100	97
	30.	100	100	100	100	100	100	100	100	99
	60.	100	100	100	100	100	100	100	100	100

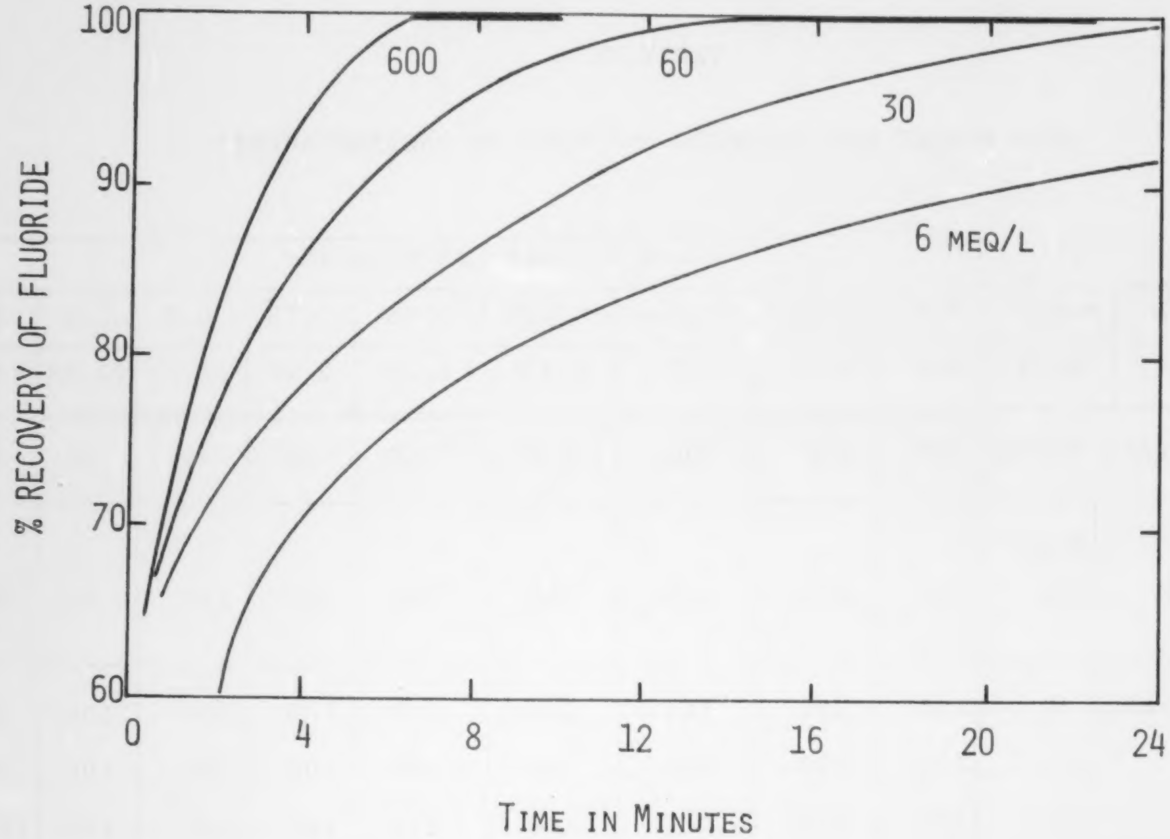


FIGURE 6

RATE OF FLUORIDE RECOVERY WITH CITRATE

(FROM STANDARD SOLUTIONS CONTAINING
5×10^{-5}M FLUORIDE AND 0.5 MG/L ALUMINUM)

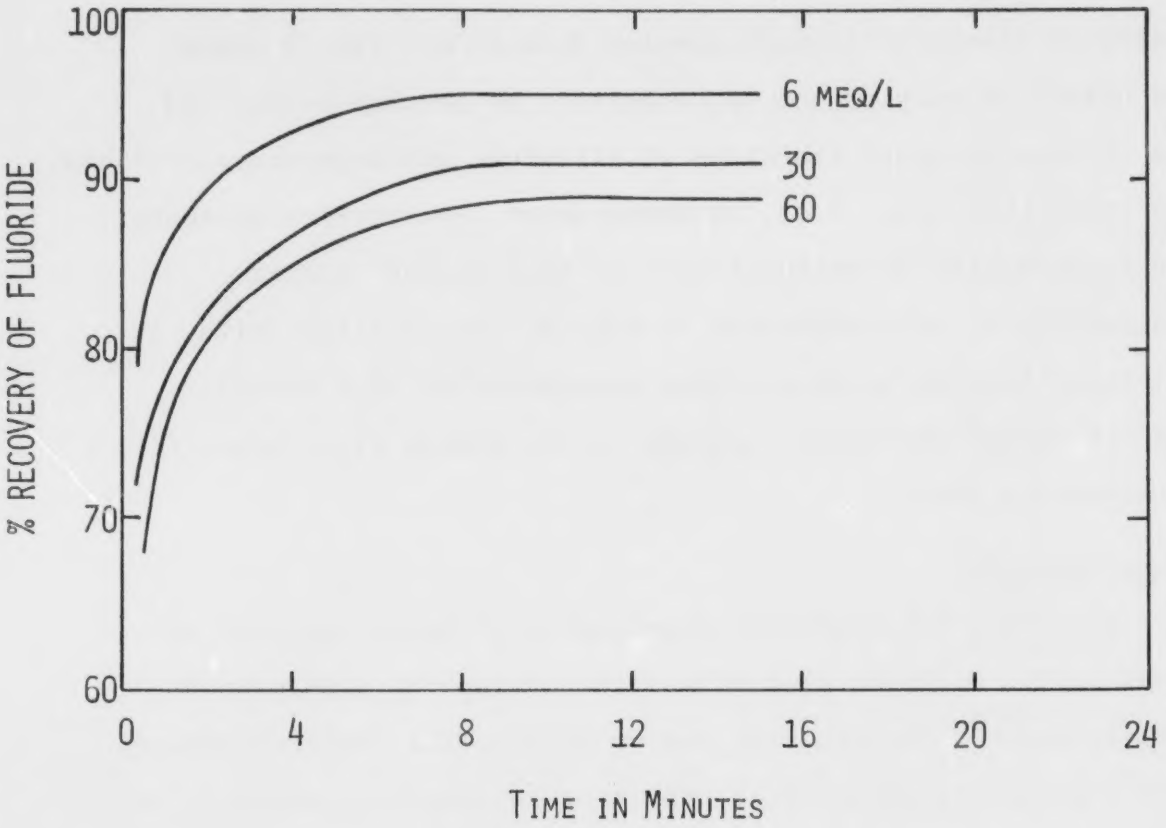


FIGURE 7

RATE OF FLUORIDE RECOVERY WITH CDTA

(FROM STANDARD SOLUTIONS CONTAINING
5×10^{-5}M FLUORIDE AND 0.5 MG/L ALUMINUM)

the added buffer does not disturb the original distribution of fluorides in the test solution; i.e., free versus complexed. This can be determined by examining the effect of acetate buffer on aluminum-fluoride complex formation. Fig. 8 shows the effect of varying the concentration of acetate buffer and the release of bound fluorides at different aluminum concentrations. The ideal condition, i.e., no measurement interference by acetate, can be estimated by extrapolation to zero acetate buffer concentration, as illustrated in Fig. 8. As an alternative, it was found that an optimum buffer concentration of 0.1M will provide enough buffering capacity to the system with insignificant interference effect.

Total Fluorides

Selective ion electrode measurement of total fluoride is based on the addition of 0.1M acetate buffer and 0.2M citrate masking agent. In both free and total fluoride measurements, the test solution is adjusted to 0.5M ionic strength by adding sodium nitrate.

A stepwise procedure applicable to the analysis of fluorides in drinking water is shown in Fig. 9. This procedure was used for characterizing fluorides in the City of Ann Arbor, Michigan water supply. Typical examples are shown in Table V.

Continuous Monitoring

It was proposed that fluorides in drinking water be continuously measured simply by immersing a fluoride electrode and a reference electrode in the sample stream.[31,32] This technique is subject to numerous limitations. It does not account

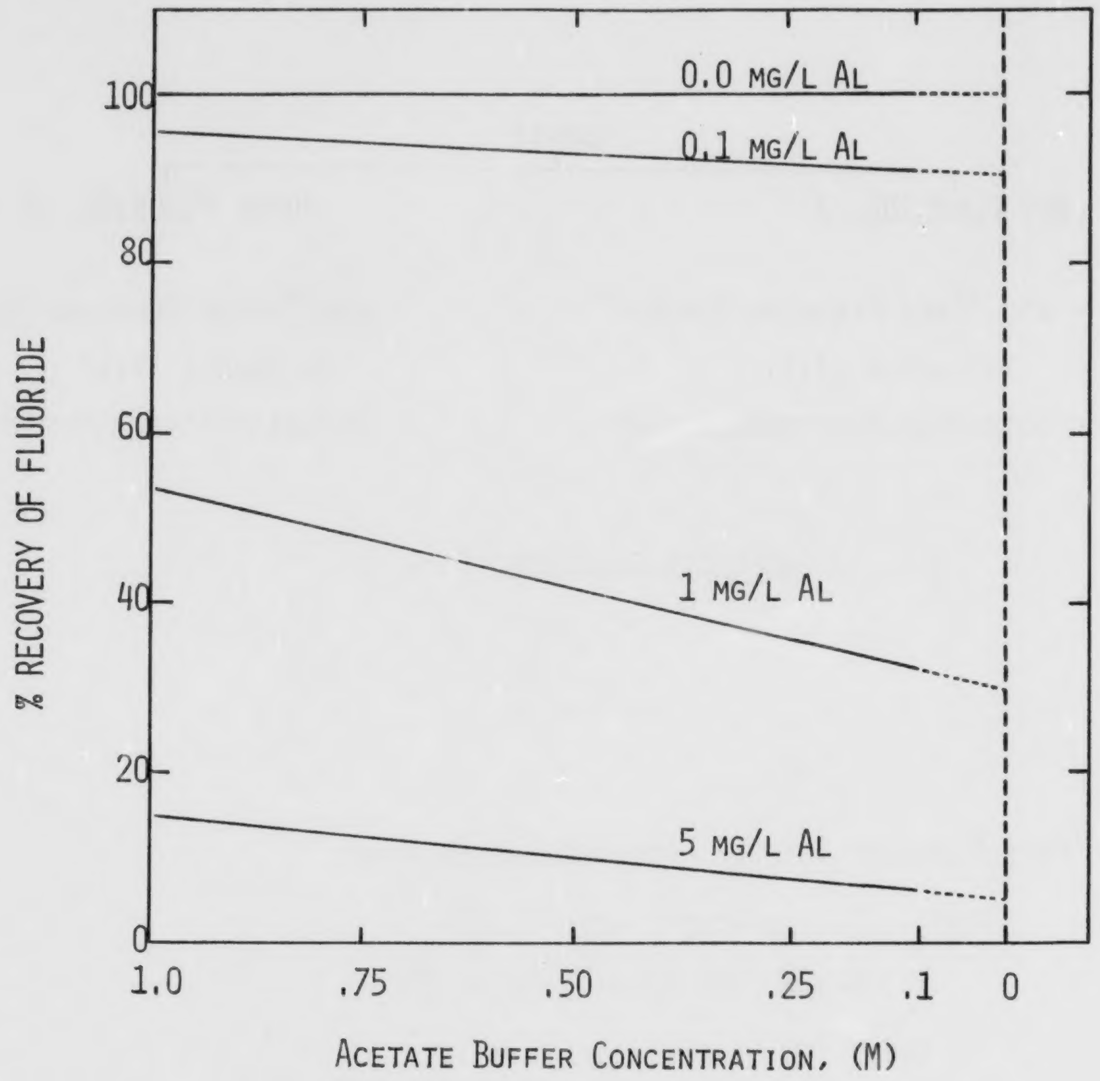


FIGURE 8

EFFECT OF ACETATE BUFFER ON FREE FLUORIDE MEASUREMENT

(standard solutions containing 5×10^{-5}M fluoride and variable aluminum concentrations)

SAMPLE

FREE FLUORIDE, A	TOTAL FLUORIDE, B
- ADD "FREE FLUORIDE BUFFER"* TO SAMPLE (1:1)	- ADD "TOTAL FLUORIDE BUFFER"† TO SAMPLE (1:1)
- POTENTIOMETRIC MEASUREMENT	- POTENTIOMETRIC MEASUREMENT

COMPLEXED FLUORIDE, C = B - A

*FREE FLUORIDE BUFFER: PREPARED AS FOLLOWS:

ADD 5.7 ML ACETIC ACID (0.1M)
84.99 G SODIUM NITRATE (1.0M)

TO ABOUT 700 ML REDISTILLED WATER. ADJUST THE pH TO 5.2 WITH CONCENTRATED NaOH SOLUTION, AND VOLUME TO 1.0 LITER.

†TOTAL FLUORIDE BUFFER: SAME AS ABOVE, BUT IN ADDITION ADD SODIUM CITRATE AS MASKING AGENT, 58.8 G/L (0.2M).

FIGURE 9

SCHEMATIC ILLUSTRATION FOR CHARACTERIZATION OF FLUORIDES IN DRINKING WATER

TABLE V

CHARACTERIZATION OF FLUORIDE IN ANN ARBOR, MICHIGAN WATER SUPPLY

Date	Total, mg/l	Free, mg/l	Complexed
October 5, 1970	0.53	0.49	7.5%
October 15, 1970	0.33	0.29	9.1%
October 4, 1970	0.64	0.59	7.8%
November 6, 1970	0.50	0.43	14.0%
March 9, 1971	0.94	>0.93	<1.0%
March 22, 1971	0.98	0.97	1.0%
April 6, 1971	0.97	0.96	1.0%

for the pH effect and changes in ionic strength, as described earlier. In order to get meaningful measurements using this procedure, correction factors must be applied to account for both the pH and ionic strength effects. In addition to being a tedious procedure subject to numerous errors, measurements under these conditions should be limited to free fluorides.

A system for monitoring free and total fluorides is shown schematically in Fig. 10. Acetate buffer and sodium nitrate are added to a stream of water to adjust the pH to 5.2 and ionic strength to about 0.5M, after which free fluorides are measured with the fluoride electrode system. This step is followed by the addition of citrate masking agent, and measurement of total fluorides with a second fluoride electrode. Mixing for about ten minutes in required after addition of the masking agent and before measuring total fluoride.

Conclusions

Application of the lanthanum fluoride selective ion electrode for fluoride measurement in drinking water has been described in the recent literature,[16,17,18,19,20] and was recently included in Standard Methods.[33] The proper use of this technique is based on understanding the modes of interferences with the selective ion electrode measurement and fluoride complex formation in the test solution. These points are not clearly defined in the previous literature.

Data obtained in this study indicate that for electrode measurement of fluorides in the range commonly found in drinking

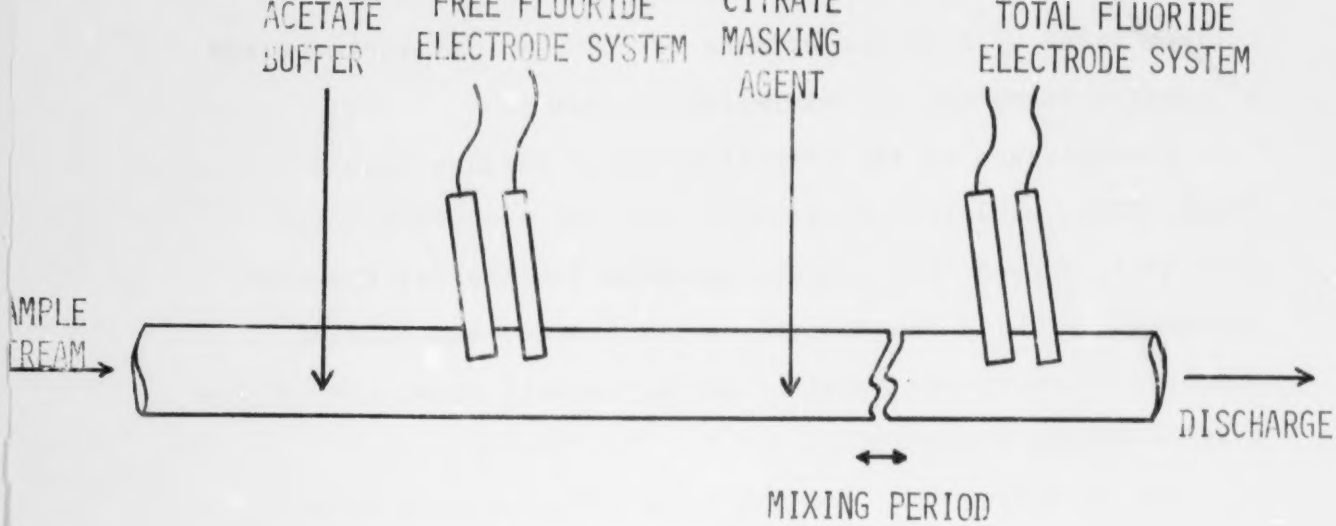


FIGURE 10

SCHEMATIC ILLUSTRATION OF FREE AND TOTAL FLUORIDE MONITOR water, the pH of the test solution should be adjusted to an optimum value of 5.2; the effects of both OH^- interference and H^+ complex formation are minimized at this pH.

A comparison of the effectiveness of masking agents (EDTA, CDTA, oxalate and citrate) used for measuring total fluorides, showed that citrate provides the highest fluoride recovery. At high concentrations of citrate, the rate of fluoride recovery was found to be the fastest among the various masking agents evaluated.

The lanthanum fluoride ion selective electrode offers a unique advantage in the characterization of free, total and complexed fluorides in drinking waters. A simple procedure was developed and evaluated on Ann Arbor drinking water over a period of several months. The results of this evaluation indicate that the percentage of complexed fluorides delivered to the consumer may amount to 14% of the total fluorides present.

A continuous monitoring system for the determination of free and total fluoride was described, using reagent addition for pH, ionic strength adjustment and recovery of complexed fluorides.

References

1. McClure, Frank J. Water Fluoridation: The Search and the Victory. U. S. Department of Health, Education and Welfare, National Institute of Dental Research, Bethesda, Maryland (1970).
2. Maier, Franz J. 25 Years of Fluoridation. J. AWWA, 62:3 (Jan. 1970).
3. Zipkin, I. & McClure, F.J. Fluoride Drinking Waters. USDEW, Public Health Service Publication No. 825 (1962). p. 483.
4. Hein, J.W., Gardner, D.E. & Haydon, G.B. Preliminary Investigations of the Effect of Sodium Monofluorophosphate on Salivary Acid Production and Hydroxy Apatite Solubility. Journal Dental Res., 30:466 (1951).
5. Kempf, C.A., Greenwood, D.A. & Nelson, V.E. Studies Relating to the Toxicity of Fluorine Compounds. J. Lab. Clin. Med., 22:1133 (1937).
6. Boyer, P.D., Evans, R.J. & Phillips, P.H. The Toxicity and Effect of Certain Fluoridated Derivatives of Phenylalanine and Tyrosine on Basal Metabolic Rate. J. Pharmacol. and Exper. Therap., 73:176 (1941).
7. Cooley, W. E. Reaction of Tin (II) and Fluoride Ions with Etched Enamel. J. Dental Res., 40:1199 (1961).
8. Brudevold, F., Steadman, L.T., Gardner, L.T., Rowley, D.E. & Little, F.M. Uptake of Tin and Fluoride by Intact Enamel. J. Am. Dental Assn., 53:159 (1956).

9. Cooley, W.E. Applied Research in the Development of Anticarris Dentifrices. *J. Chem. Educn.*, 47:177 (1970).

10. Durst, R.A. & Taylor, J.K. Modification of the Fluoride Activity Electrode for Microchemical Analysis. *Anal. Chem.*, 39:1483-5 (1967).

11. Singer, L. & Armstrong, W.D. Determination of Fluoride in Bone with the Fluoride Electrode. *Anal. Chem.*, 40:613-4 (1968).

12. Lingane, J.J. A Study of the Lanthanum Fluoride Membrane Electrode for End Point Detection in Titrations of Fluoride with Thorium, Lanthanum and Calcium. *Anal. Chem.*, 39:881 (1967).

13. Lingane, J.J. Further Study of the Lanthanum Fluoride Membrane for Potentiometric Determination and Titration of Fluoride. *Anal. Chem.*, 40:935 (1968).

14. Durst, R.A. Fluoride Microanalysis by Linear Null-Point Potentiometry. *Anal. Chem.*, 40:931 (1968).

15. Serinivasan, K. & Rechnitz, G.A. Reaction Rate Measurements with Fluoride Ion Selective Membrane Electrode: Formation Kinetics of Ferrous Fluoride and Aluminum Fluoride Complexes. *Anal. Chem.*, 40:1818-25 (1968b).

16. Frant, M.S. & Ross, J.W. Electrode for Sensing Fluoride Ion Activity in Solutions. *Science*, 154:1553 (1966).

17. Frant, M.S. & Ross, J.W. Use of a Total Ionic Strength Adjustment Buffer for Electrode Determination of Fluoride in Water Supplies. *Anal. Chem.*, 40:1169 (1968).

18. *Orion Instruction Manual*. (2nd Ed., 1967) Fluoride Ion Activity Electrode, Model 94-09. Orion Research, Inc., Cambridge, Mass.

19. Andelman, J.B. Ion Selective Electrodes - Theory and Applications in Water Analysis. *J. Water Pollution Control Federation*, 40, (11) (Pt. 1), 18444-60, (Eng) (1968).

20. Bock, R. & Strecker, Fresenius Z. Direkte Electrometrische Bestimmung des Fluorid-Ions. *Anal. Chem.*, 234:322 (1968) (Ger).

21. Durfor, Charles N. & Becker, Edith. Public Water Supplies of the 100 Largest Cities in the United States, 1962. U. S. Geological Survey Water Supply Paper 1812, U. S. Government Printing Office, Washington, D. C. (1964).

22. Riseman, Jean M. Specific Ion Electrodes - Versatile New Analytical Tools. *Industrial Wastes*, p.12 (Sept.-Oct. 1970).

23. Harwood, J.E. The Use of an Ion Selective Electrode for Routine Fluoride Analysis on Water Samples. *J. Water Research*, 3:273 (1969).

24. Mesmer, R.E. Lanthanum Fluoride Electrode Response in Aqueous Chloride Media. *Anal. Chem*.,40:443 (1968).

25. Rechnitz, G.A. Ion Selective Electrodes. *Chem. & Engrg. News*, 45 (25), 146 (1967).

26. Scrinivasan, K. & Rechnitz, G.A. Activity Measurements with a Fluoride-Selective Membrane Electrode. *Anal. Chem.*, 40:509 (1968).

27. Ciavatta, L. Hydrolysis of Fluoride Ion, F^-, in 3M Na^+ (ClO_4^-) and 3M K^+ (Cl^-, F^-) Media. Arkiv Kemi, 21:129 (1963).

28. Butler, James Newton. Ionic Equilibrium, A Mathematical Approach. Addison-Wesley Publishing Co., Inc. (1964) Chapter 5-1, p. 115.

29. Bauman, E.W. Determination of Aluminum by Potentiometric Titration with Fluoride. Anal. Chem., 42:110 (1970).

30. Crosby, N.T., Dennis, A.L. & Stevens, J. G. An Evaluation of Some Methods for the Determination of Fluoride in Potable Waters and Other Aqueous Solutions. Analyst, 93:643 (1968).

31. Babcock, R.H. & Johnson, D.A. Selective Ion Electrode System for Fluoride Analysis. J. AWWA (Aug. 1968) p. 953.

32. Orion Research Incorporated. The ABC's of Monitoring. Newsletter/Specific Ion Electrode Technology (May/June 1970).

33. Standard Methods for Examination of Water and Wastewater. (13th Ed., 1971), American Public Health Association, American Water Works Association, Water Pollution Control Federation.

This study was supported in part by Division of Water Hygiene, EPA, Research Grants No. 1 RO1 EC 00318-01 and -02.

3.0 CHARACTERIZATION OF CALCIUM CARBONATE SATURATION EQUILIBRIUM

3.1 GENERAL

Calcium carbonate saturation equilibrium, the "stability" of a water, is a measure of the reversible pipe scaling process. Characterization of this parameter has been attempted by many investigators. "Stability index" is a number which refers to the tendency of a water to deposit - or corrode - a scale of calcium carbonate at the surface of a pipe. Inhibition of corrosion in iron pipes by calcium carbonate films has been reported by Larson,[17] Stumm,[18] Mancy[19] and McClanahan.[20] The corrosion protection afforded by a thin hard film of calcium carbonate, and the deleterious effects of a thick bulbous film on the hydraulic carrying capacity of a distribution main are equally apparent. Ideally, water in a distribution system should form a thin hard film which is not permeable to corrosive elements in the water.

3.2 THEORY

3.21 EQUILIBRIUM CONSIDERATIONS

A water which is oversaturated or undersaturated with respect to calcium carbonate tends to undergo chemical change and approach a state of equilibrium. This tendency can be expressed by the change in free energy, ΔG, for the following reactions:

$$CaCO_3\ (s) \rightarrow Ca^{2+} + CO_3^{\ 2-}\ ;\ \Delta G = RT\ \ln \frac{[Ca^{2+}][CO_3^{\ 2-}]}{K_s} \qquad (3.1)$$

$$CaCO_3\ (s) + H^+ \rightarrow Ca^{2+} + HCO_3^{\ -}\ ;$$

$$\Delta G = RT\ \ln \frac{[Ca^{2+}][HCO_3^{\ -}]}{K_s\ [H^+]} \qquad (3.2)$$

$$CaCO_3\ (s) + H_2CO_3^{\ *} \rightarrow Ca^{2+} + 2HCO_3^{\ -};$$

$$\Delta G = RT\ \ln \frac{[Ca^{2+}][HCO_3^{\ -}]^2 K_2}{K_1 K_s [H_2CO_3^{\ *}]} \qquad (3.3)$$

where K_1, K_2 are the first and second acidity constants for $H_2CO_3^{\ *}$, and K_s is the solubility product of calcite. $[H_2CO_3^{\ *}]$ refers to the sum of $[H_2CO_3]$ and $[CO_2]_{aq}$. For oversaturated waters, ΔG is negative; for undersaturation, ΔG is positive.

It has been common to characterize the degree of departure from calcium carbonate equilibrium conditions by pH measurements. The H^+ activity of the water sample is correlated with a hypothetical value of H^+ activity, expressed as follows:

$$[H^+]_{eq.} = \frac{[Ca^{2+}]_{act.}\ [HCO_3^{\ -}]_{act.}}{K_s/K_2} \qquad (3.4)$$

or, "the calculated hydrogen ion activity at which, without change in total alkalinity and calcium content, a water would be in equilibrium with solid calcium carbonate."[5] Accordingly, when $[H^+]_{meas} > [H^+]_{eq}$, the water is aggressive with respect to $CaCO_3$, and when $[H^+]_{meas} < [H^+]_{eq}$, the water will deposit $CaCO_3$.

Langelier[21] proposed using the difference between measured pH and the calculated equilibrium pH values as a measure of the stability of a water. The term "saturation index" (SI) was defined as follows:

$$SI = pH_{meas} - pH_{eq} \tag{3.5}$$

where pH_{eq} can be defined from equation 3.4 as:

$$pH_{eq} = \log\left({}^{K_s}/_{K_2}\right) - \log\,[Ca^{2+}]_{act} - \log\,[HCO_3^-]_{act} \tag{3.6}$$

The concentration of HCO_3^- can be calculated from analytically determinable parameters, e.g.:

$$[HCO_3^-] = \frac{[Alky]_T - {}^{K_w}/_{[H^+]} + [H^+]}{(1 + {}^{2K_2}/_{[H^+]})} \tag{3.7}$$

and

$$[HCO_3^-] = X_1 C_T \tag{3.8}$$

where C_T is the analytical concentration for total carbonates and

$$X_1 = \frac{[HCO_3^-]}{C_T} \tag{3.9}$$

Within the pH range of many natural waters (7.5 to 9.0), X_1 is close to unity and $[HCO_3^-] \simeq C_T$. Below pH 8.3,

$$[HCO_3^-] = [Alky]_T \tag{3.10}$$

Corrections for ionic strength (μ) were added to this equation by Larson and Buswell[22]:

$$pH_{eq} = \log\left({}^{K}s/{}_{K_2}\right) - \log\,[Ca^{2+}]_{act} - \log[\mathrm{Alky}]_T + 9.30 + \frac{2.5\sqrt{\mu}}{5.5\mu + 5.3\sqrt{\mu} + 1} \qquad (3.11)$$

Accordingly, from Equation (3.5), a positive saturation index indicates a scale forming water; a negative index indicates a scale dissolving water.

Another parameter, the "stability index" (S), proposed by Ryzner[23], supports the equilibrium pH value:

$$S \;=\; 2pH_{eq} \overset{-\ \text{minus}}{\cancel{+}} pH_{meas} \qquad (3.12)$$

According to Ryzner, whose work was largely empirical and based on weight gains of coupons in a test water, waters with a stability index of approximately 7.5 or less are scale forming; waters with indices above 7.5 to 8.0 are increasingly scale dissolving. This index provided some information about the amount of scale which might be expected from a water; however, there was no attempt to correlate the index with corrosive waters.

3.22 KINETIC CONSIDERATIONS

Calculation of the calcium carbonate stability index, using either Equation (3.5) or (3.12), has been widely applied in the water treatment industry. However, there are several limitations to this procedure. First, such a calculated index provides information only about the degree of deviation from the equilibrium condition; i.e., the directional tendency of a water to deposit or dissolve a calcium carbonate film. Kinetic aspects of water stabilization or rates of attainment of equilibrium are not included. Thus, the rate and amount of calcium carbonate deposited or dissolved cannot be predicted from such equilibrium data. It has been demonstrated experimentally that, in the absence of crystallization nuclei, oversaturated solutions of calcium carbonate may remain oversaturated for years.[24,25,26] Also, the presence of Mg^{2+}, polyphosphates, or dissolved organic matter (present in most water supplies) influences the rate of calcium carbonate precipitation or dissolution dramatically.

The effect of Mg^{2+} on the rate of calcium nucleation was studied by Pytkowicz.[24] These studies indicate that magnesium-free artificial sea water yields much shorter times of nucleation (in the order of minutes) than natural sea waters (in the order of several hours). Enrichment of water samples with magnesium was found to decrease dramatically the rate of calcium carbonate nucleation. This was explained as a result of formation of magnesium carbonate complexes, which exhibit high stability with higher alkalinity. These complexes are very effective in inhibiting calcium carbonate crystal formation.

Polyphosphates and trace organics interfere with the rate of calcium carbonate deposition because of their tendency to form complexes, thus causing a sequestering effect which keeps the calcium ions in solution. This effect can easily be demonstrated by comparing results of Ca^{2+} determinations using a calcium ion selective electrode and the EDTA titration technique. The former technique gives a measure of the free Ca^{2+} and the latter, total Ca^{2+} concentration. It has been demonstrated in this study that ion selective electrode measurements are approximately equal to 80% to 90% of EDTA titrations for municipal water supplies. This suggests that not all of the calcium present in the water supply is in the free ionic form, but rather distributed between the free form and a fraction which exists as solubilized complexes, generally organo or phospho in nature.

3.3 EXPERIMENTAL

To the water treatment plant operator, stability is an important consideration. If a continuous or rapid batch test were available for the determination of this parameter, the operator could adjust the treatment process to improve the quality of the protective film in the distribution system.

In 1939, Enslow proposed[27,28] a continuous stability indicator which was, at the time, expected to fulfill these requirements. A stream of water was continuously but slowly passed through a column of powdered chalk. The pH and titratable alkalinity were measured before and after contact in the column. Changes in these parameters were related to the corrosivity or scale forming capacity of the test water. A contact time of two hours was considered sufficient for the water to be in complete equilibrium with calcium carbonate. Data obtained in this project do not support this conclusion.

An apparatus similar to Enslow's column was constructed, as shown in Fig. 3-1. The column is a 24 inch length of 3 inch i.d. plastic pipe. Test water was recirculated through the column using a peristaltic pump. The column was packed either with marble (calcium carbonate) chips or powdered calcium carbonate. An ion selective electrode capable of monitoring the hardness of influent and effluent water was included in the apparatus. Data shown in Tables 3-I and 3-II are some of the results of experiments with the calcium carbonate column stability index monitor. Changes in pH, even with low flows and high recirculation rates, were very small. These changes did not approach the hypothetical pH_{eq}. Changes in hardness were negligible.

Failure of this system to produce data which might be useful as a stability index suggested that very long contact times were required for the water to come into equilibrium with calcium carbonate. A second experiment was designed to study the rate of calcium carbonate equilibrium in various waters in contact with different forms of calcium carbonate. A batch system was used in which waters of

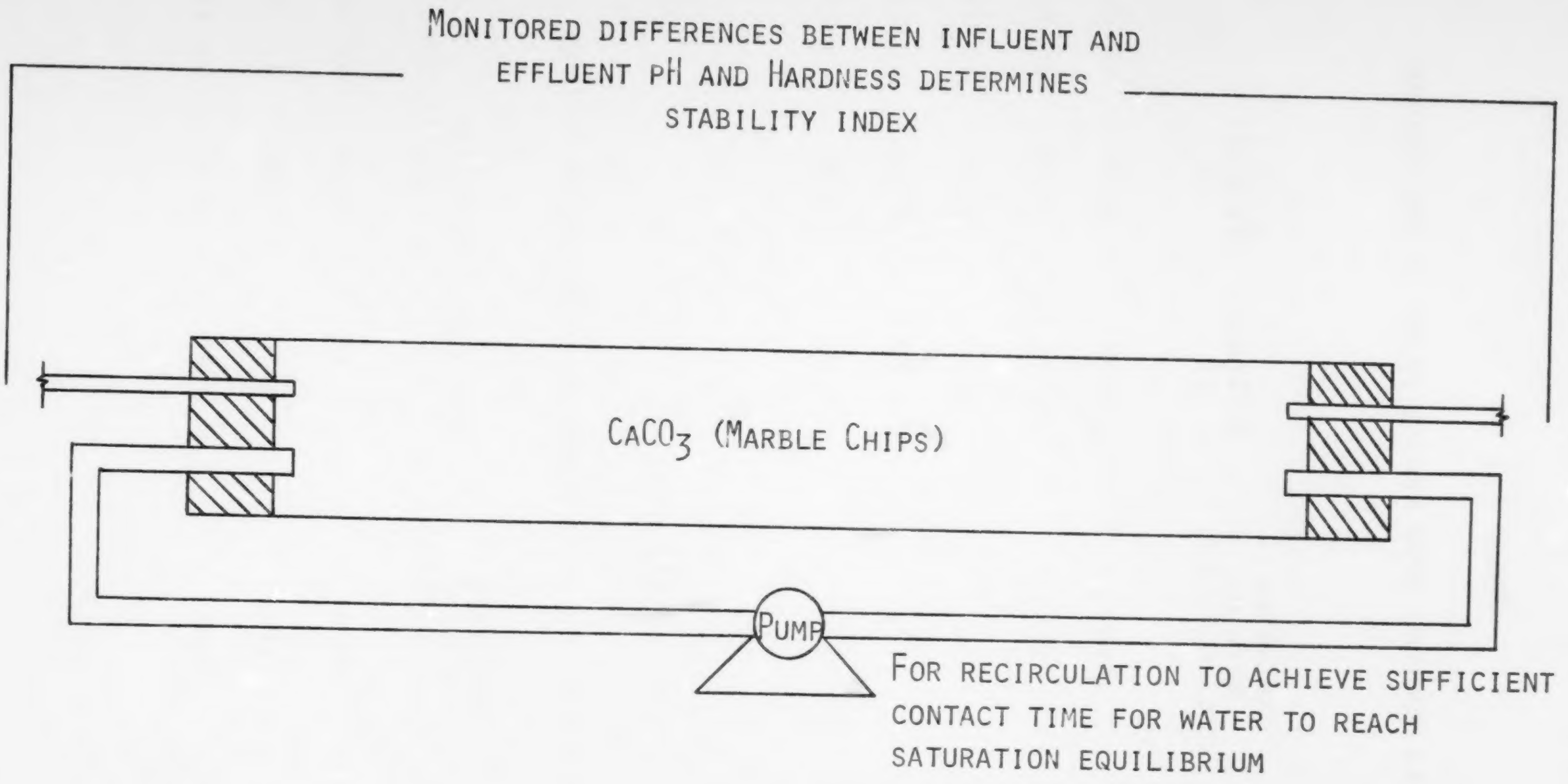

MONITORED DIFFERENCES BETWEEN INFLUENT AND EFFLUENT pH AND HARDNESS DETERMINES STABILITY INDEX
$CaCO_3$ (MARBLE CHIPS)
PUMP
FOR RECIRCULATION TO ACHIEVE SUFFICIENT CONTACT TIME FOR WATER TO REACH SATURATION EQUILIBRIUM

FIGURE 3-1. STABILITY INDEX MONITOR FOR SATURATION EQUILIBRIUM MEASUREMENT

TABLE 3-I

STABILITY INDEX MONITOR WITH MARBLE CHIPS IN THE COLUMN

Rate of Flow Thru System, ml/min.	Relative Rate of Recirculation	Influent pH	Effluent pH	ΔpH
18.5	None	9.94	9.73	-0.21
20.0	1.0	10.00	9.80	-0.20
74.0	1.1	9.83	9.78	-0.05
33.5	1.4	9.93	9.80	-0.13
34.0	1.6	9.91	9.71	-0.20

TABLE 3-II

STABILITY INDEX MONITOR WITH POWDERED $CaCO_3$ IN THE COLUMN

Rate of Flow Thru System, ml/min.	Relative Rate of Recirculation	Influent pH	Effluent pH	ΔpH
54.0	None	9.85	9.65	-0.20
7.5	None	9.88	9.65	-0.23
2.0	None	9.80	9.36	-0.44

defined chemical characteristics were mixed at constant rates with marble chips or pure powdered calcium carbonate. Temperature of the test samples was controlled in a water bath at 25° ± 0.2°C. Hardness and pH were measured with respect to time using a glass pH electrode and an Orion divalent cation selective electrode.

Typical results of these experiments are shown in Figs. 3-2, 3-3, 3-4, and 3-5, and analyses of these and several other test samples are given in Table 3-III. Figs. 3-2 and 3-3 indicate the change of pH and [Ca^{2+}] of distilled water in contact with marble chips and calcium carbonate powder, respectively.

These results indicate that attainment of equilibrium is asymptotic. The data also indicate that pH changes do not follow closely the changes in [Ca^{2+}]. This can be a result of: (1) the differences in the response characteristics of the divalent cation electrode as the pH decreases and changes the availability of free Ca^{2+} for sensing by the electrode, or (2) complicated chemical transformations which cannot be explained by simple calcium carbonate equilibria relationships. In all cases, the time required to reach reasonably steady values of pH and [Ca^{2+}] was in the order of 30 to 60 hours.

The slow rate of attaining equilibrium, as shown in Figs. 3-2 through 3-5, appears to be inconsistent with the short residence times in calcium carbonate columns reported

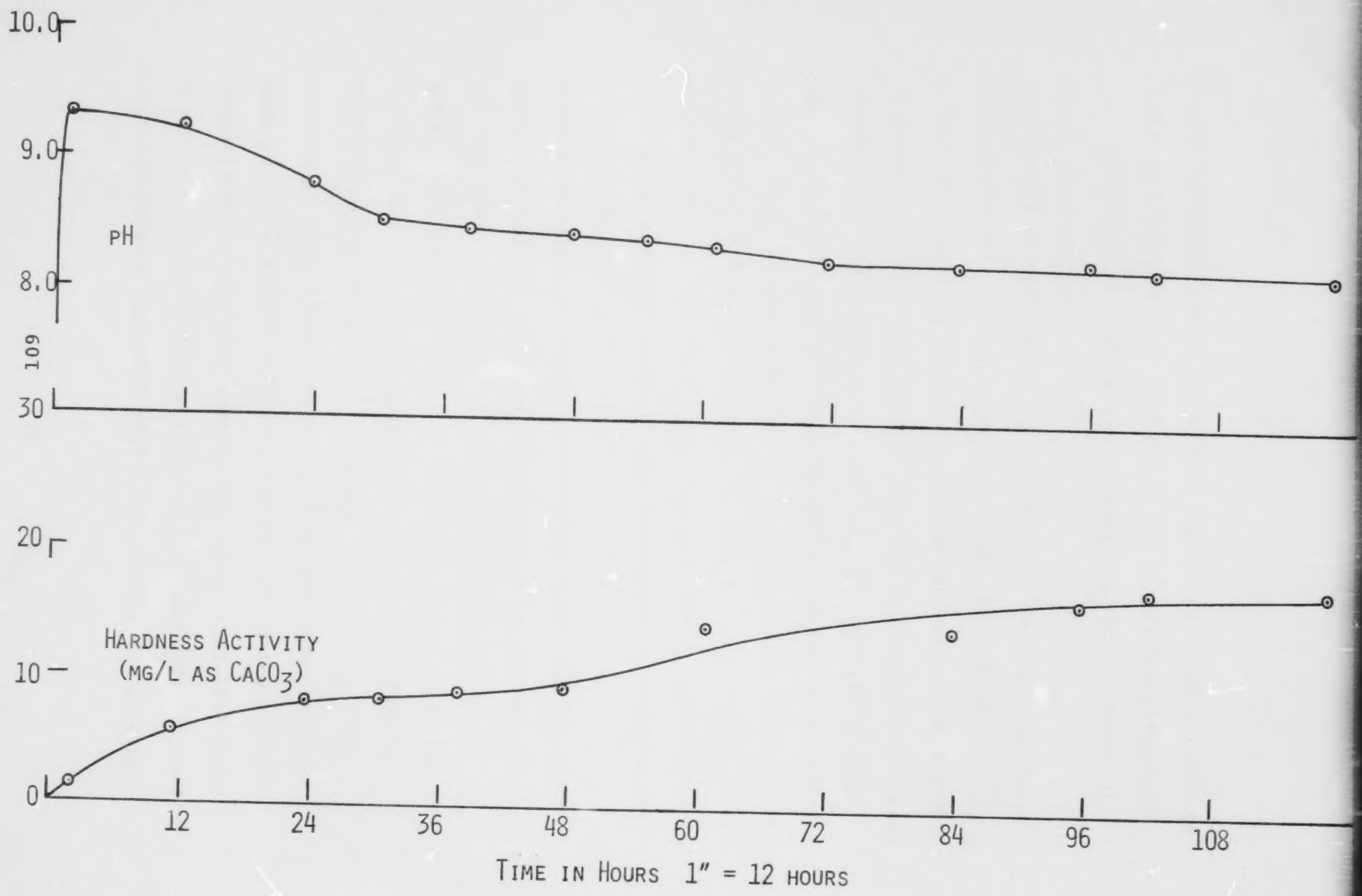


FIGURE 3-2. DISTILLED WATER IN CONTACT WITH PURE POWDERED $CaCO_3$

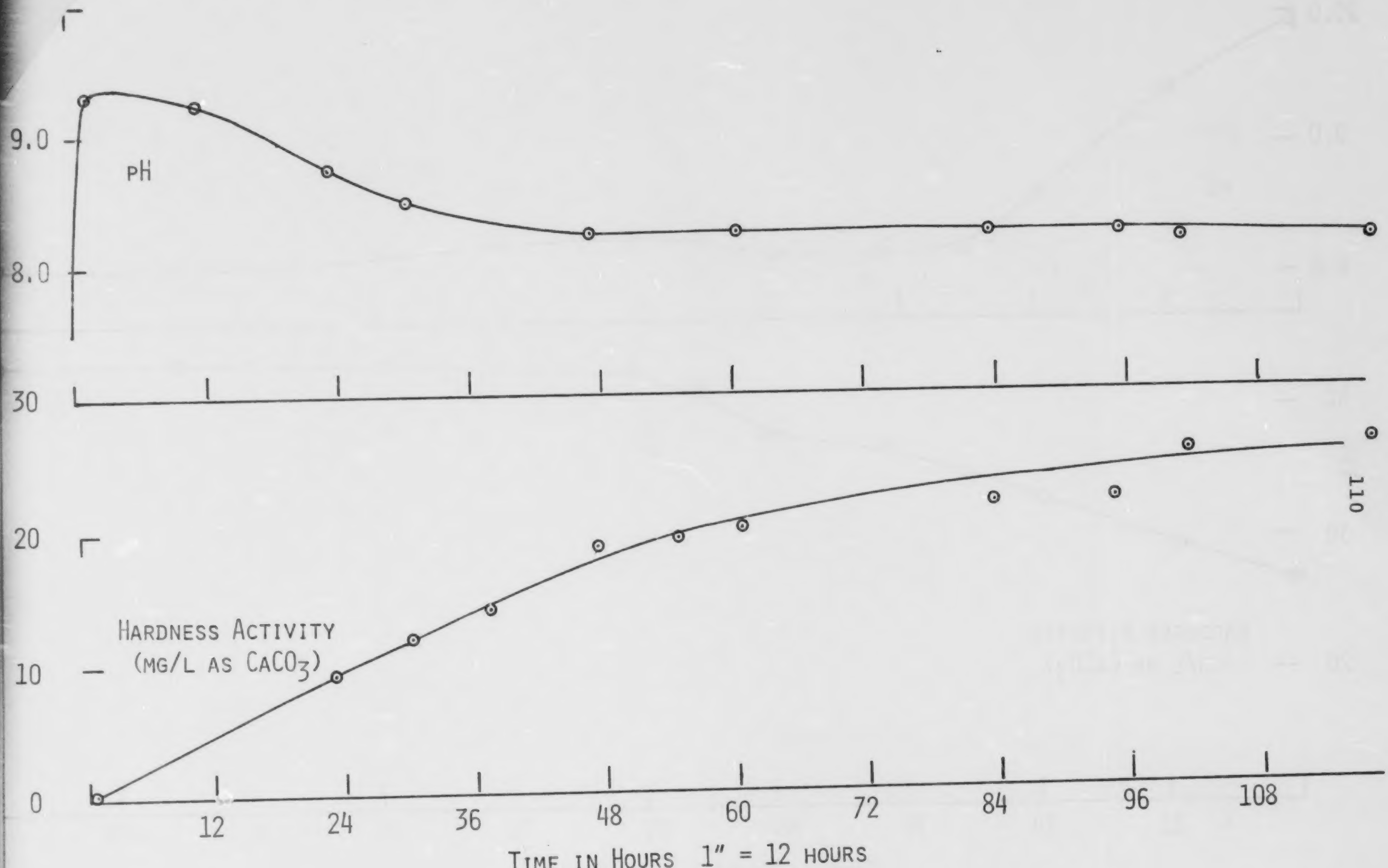


Figure 3-3. Distilled water in contact with marble chips

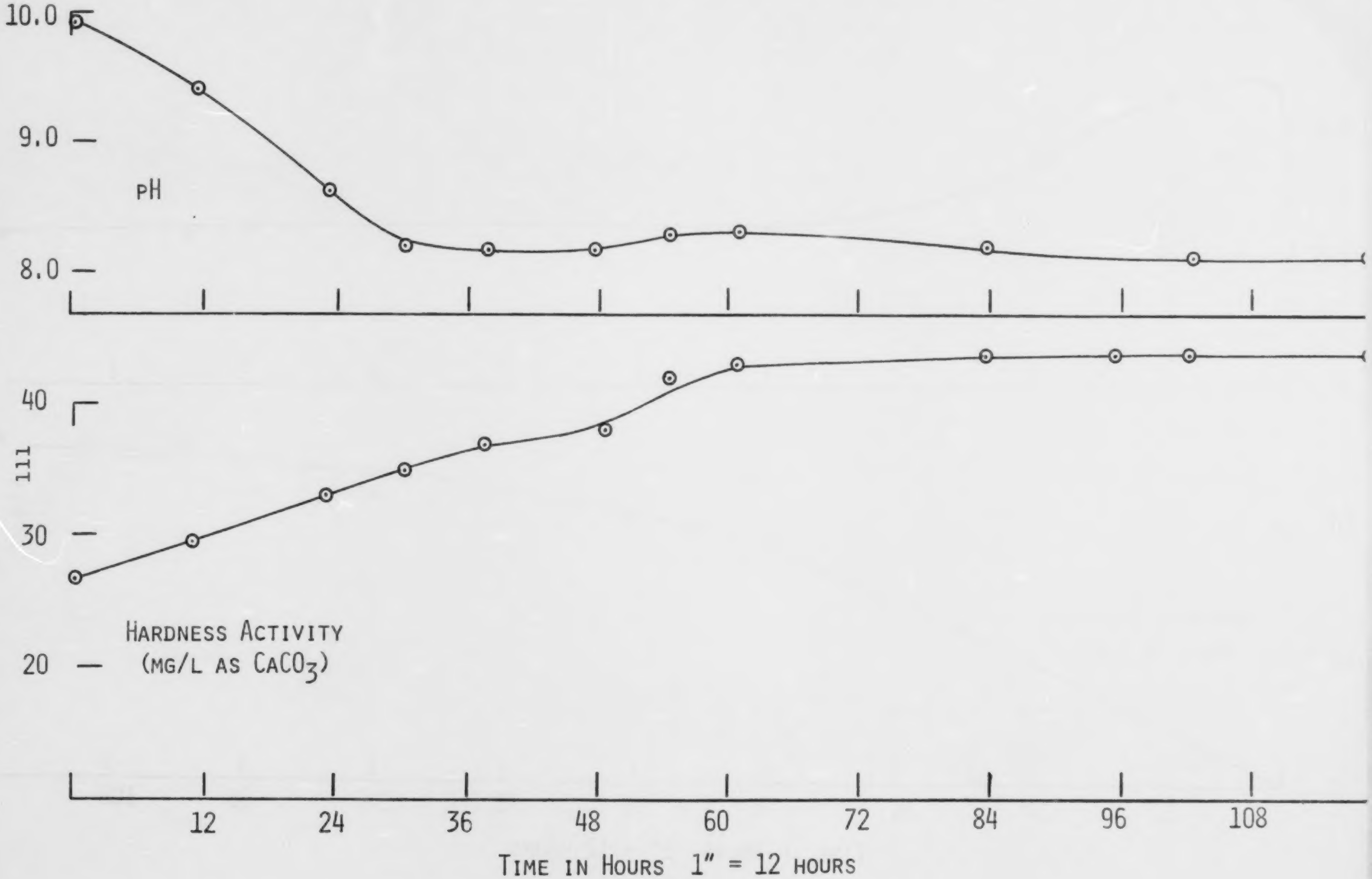


FIGURE 3-4. ANN ARBOR TAP WATER IN CONTACT WITH PURE POWDERED $CaCO_3$

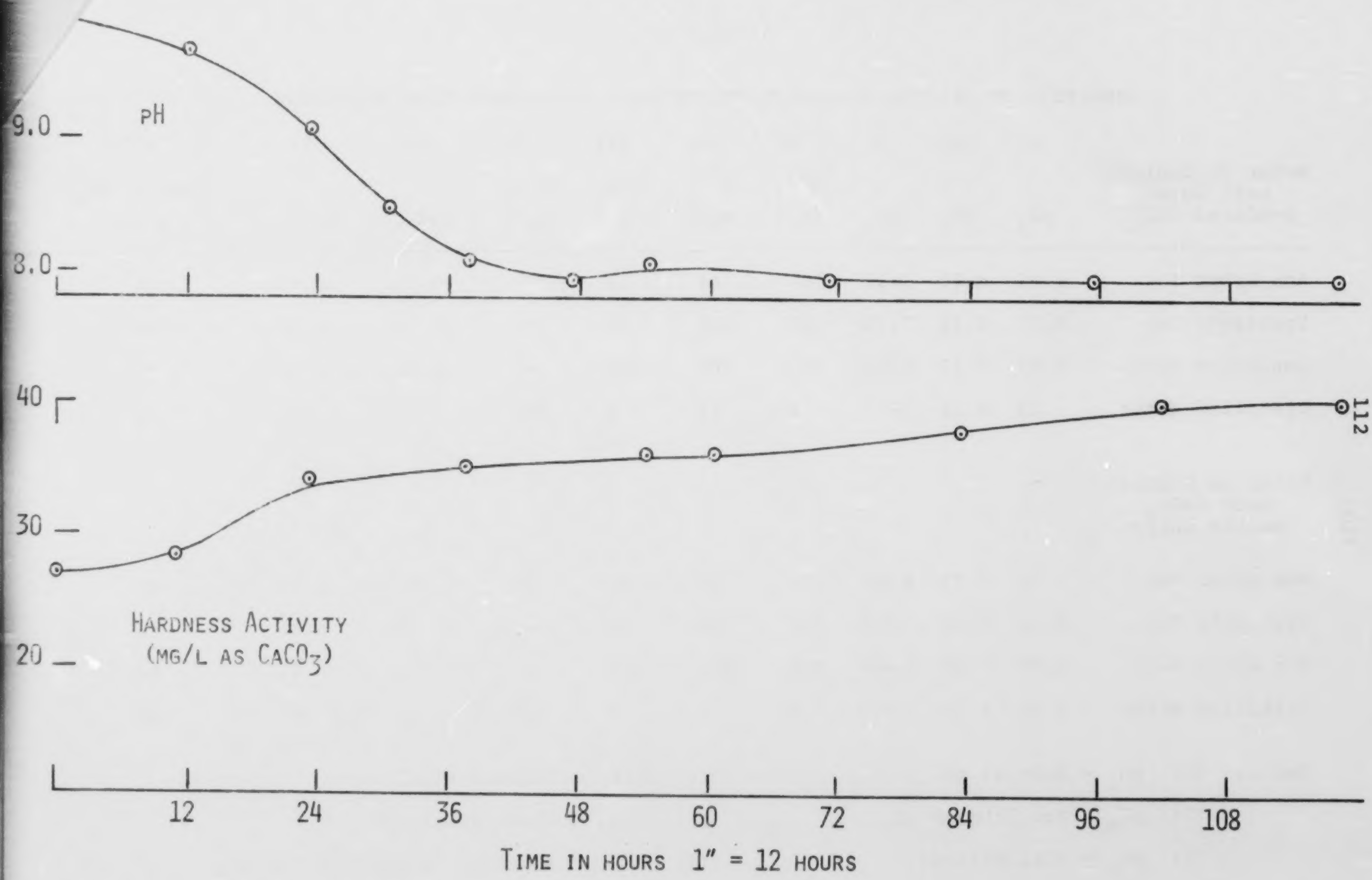


Figure 3-5. Ann Arbor tap water in contact with marble chips

TABLE 3-III

ANALYSIS OF CALCIUM CARBONATE EQUILIBRIUM EXPERIMENT TEST SOLUTIONS

Water in Contact with Pure Powdered $CaCO_3$	(1) pH_i	(2) pH_e	(3) pH_s	(4) M^{2+}_i, mg/l	(5) M^{2+}_e, mg/l	(6) Alk_i, mg/l	(7) Alk_f, mg/l	(8) $S.I._L$	(9) $S.I._R$	(10) Time to pH_e, hours
Ann Arbor Tap	9.91	8.15	8.31	27	44	34	57	+1.60	6.69	33
Ypsilanti Tap	9.35	8.20	7.75	123	131	65	--	+1.70	6.15	66
Ann Arbor Well	6.87	7.29	6.64	375	200	320	--	+0.32	6.41	44
Distilled Water	[illegible].85	8.18	--	0	17	0	52	--	--	48
Water in Contact with $CaCO_3$ Marble Chips										
Ann Arbor Tap	9.91	7.95	8.31	27	40	34	40	+1.60	6.69	48
Ypsilanti Tap	9.35	8.28	7.75	123	126	66	--	+1.70	6.15	72
Ann Arbor Well	6.87	7.28	6.64	375	230	320	--	+0.32	6.41	44
Distilled Water	5.85	8.15	--	0	26	0	52	--	--	48

Terms: (1) pH_i = Initial pH

(2) pH_e = Equilibrium pH

(3) pH_s = (Calculated)

(4) M^{2+}_i = Initial hardness

(5) M^{2+}_e = Equilibrium hardness

(6) Alk_i = Initial alkalinity

(7) Alk_f = Final alkalinity

(8) $S.I._L$ = Langlier Saturation Index

(9) $S.I._R$ = Ryzner Stability Index

by others.[27, 28] Repeated experiments indicate that the attainment of calcium carbonate saturation equilibrium under the prescribed experimental conditions is in fact a slow process. As a result of these experiments, development of a stability index monitor which requires the attainment of calcium carbonate saturation equilibrium before a result can be obtained is considered impractical.

Recent studies reported by Mancy[19] and McClanahan[20] may lead to a practical short term test for evaluating the stability of a water. McClanahan studied the role of dissolved oxygen and the mechanism of calcium carbonate film formation as they relate to corrosion of cast iron. The effect of dissolved oxygen on calcium carbonate deposition at a freely corroding cast iron rotating disc electrode can be illustrated as follows:

Anodic reaction:

$$Fe \rightarrow Fe^{2+} + 2e \qquad (3.13)$$

$$2Fe^{2+} + 5H_2O + 4HCO_3^- + 1/2\ O_2 \rightarrow 2Fe(OH)_3 + 4H_2CO_3 \qquad (3.14)$$

Cathodic reaction:

$$1/2\ O_2 + H_2O + 2e \rightarrow 2OH^- \qquad (3.15)$$

$$OH^- + Ca^{2+} + HCO_3^- \rightarrow CaCO_3\downarrow + H_2O \qquad (3.16)$$

Molecular oxygen serves as electron acceptor in the corrosion reaction. The cathodic reduction of molecular oxygen results in the localized formation of OH^- at the metal surface, which, in the presence of Ca^{2+} and HCO_3^-, results in calcium carbonate deposition. The calcium carbonate film on the surface of the corroding metal serves as a diffusion barrier for molecular oxygen, thus reducing the rate of corrosion. Equation (3.16) illustrates the dependency of $CaCO_3$ formation on the calcium hardness and alkalinity.

Mancy and McClanahan also studied the rate of formation of calcium carbonate film on platinum by the electrochemical reduction of molecular oxygen.[19,20] The structure and permeability of the deposited calcium carbonate film can be characterized by diffusion current measurement of the cathodic reduction of molecular oxygen, which is expressed as follows:

$$i_d = n\ F\ A\ \frac{Pm}{b}\ C_s \qquad (3.17)$$

where:

i_d = diffusion current for the cathodic reduction of molecular oxygen

F = the Faraday

n = number of electrons transferred per mole of oxygen

A = area of electrode surface

Pm = permeability coefficient of $CaCO_3$ film

b = $CaCO_3$ film thickness, and

C_s = dissolved oxygen content of the test water

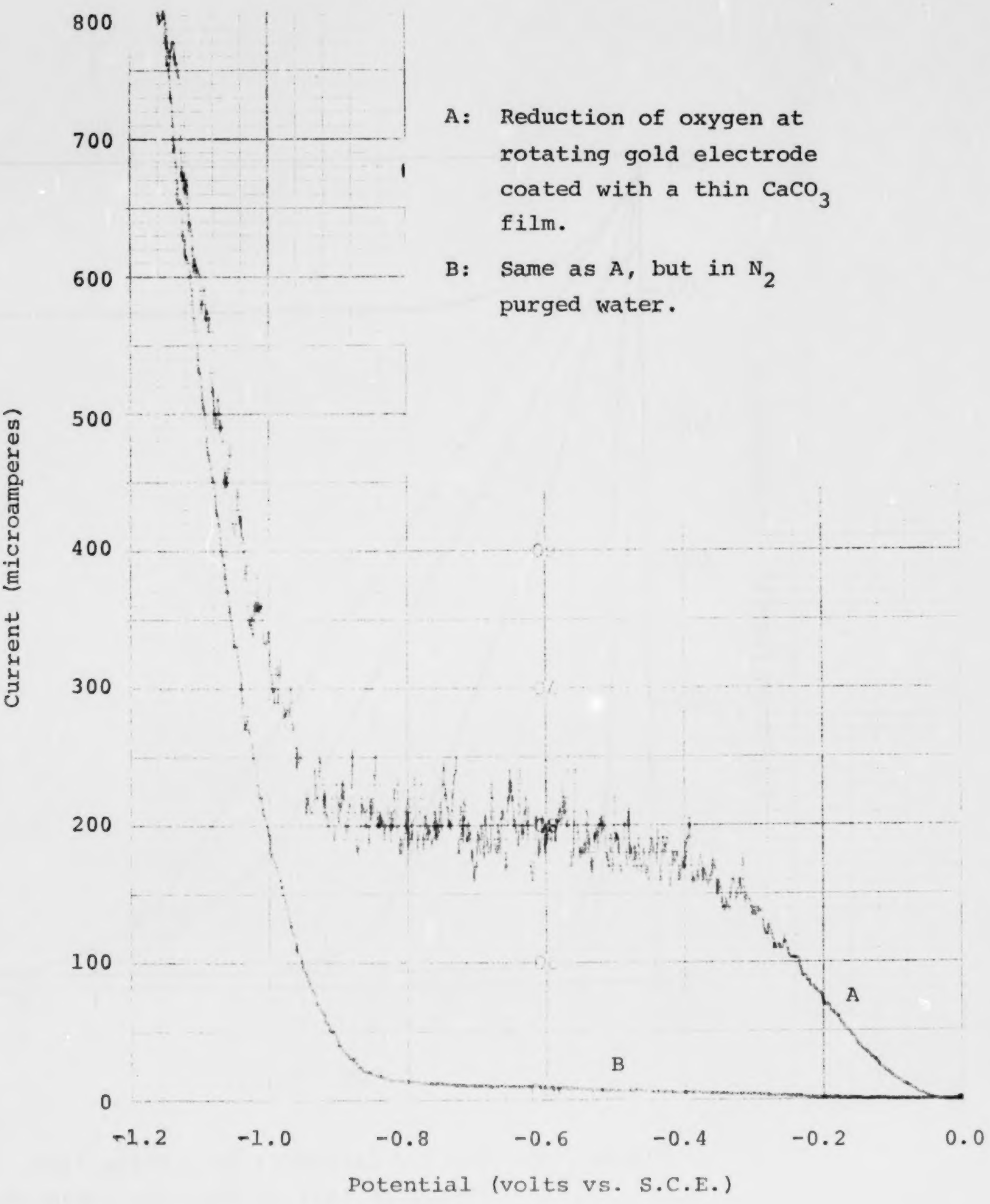
The rate of mass transport of molecular oxygen, and thus the diffusion current, are strictly dependent on the permeability and thickness of the $CaCO_3$ film when constant hydrodynamic conditions and dissolved oxygen levels in the bulk of the solution are maintained. The dependency of the rate of film formation on the initial concentrations of calcium and bicarbonate in the solution suggest a method of stability measurement which does not depend on attaining calcium carbonate saturation equilibrium. Measurement of the rate of film formation by measuring the oxygen reduction diffusion current at a rotating inert electrode is expected to provide a short term method for measuring the stability of the water, the protective quality of the film, and the rate at which the film will form in a distribution main.

This proposed Calcium Carbonate Deposition Test (CCDT) requires a three electrode measurement system similar to many modern electrochemical sensor systems. The working electrode is a rotating disc electrode upon which calcium carbonate is deposited. The counter electrode through which the current is measured is a ring which surrounds the disc. Together, the working and counter electrodes form the configuration of a rotating ring-disc electrode. The potential of the disc for the cathodic reduction of oxygen is maintained with a saturated calomel electrode. A constant temperature of 25° ± 0.2°C is maintained in a water bath.

The rotational speed of the disc was selected as a compromise between the need for maintaining constant hydrodynamics at the surface of the electrode and mixing of the bulk of the solution, and the turbulence associated with very high rotational velocities. A speed of 1600 rpm was selected as the speed at which further increases in velocity would no longer increase the diffusion current due to changes in the mass transport of oxygen to the surface of the electrode, and at which little turbulence would be created in the test solution. The potential at which the cathode is controlled (-0.9 volts vs. S.C.E.) is the potential at which the smallest change in current was observed over the largest region of change in potential. This value was established by recording the current as a function of potential sweep, as shown in Fig. 3-6.

Fig. 3-7 shows plots of the diffusion current decay for a variety of solutions with different scale formation characteristics. Analyses of these solutions, with mathematical evaluations of their scale forming tendencies, are shown in Table 3-IV. Measurement of the slope of the linear portion of these curves suggests a useful as well as rapid method of analysis.

These preliminary experiments with the rotating ring-disc electrode show a high degree of correlation between the initial solution characteristics and the rate of induced scale formation at the inert electrode. Curves 1 and 5 in Fig. 3-7 represent solutions which can easily be predicted to be scale forming; Curve 2 is clearly a corrosive water.



A: Reduction of oxygen at rotating gold electrode coated with a thin $CaCO_3$ film.

B: Same as A, but in N_2 purged water.

Figure 3-6. Current vs. potential sweep

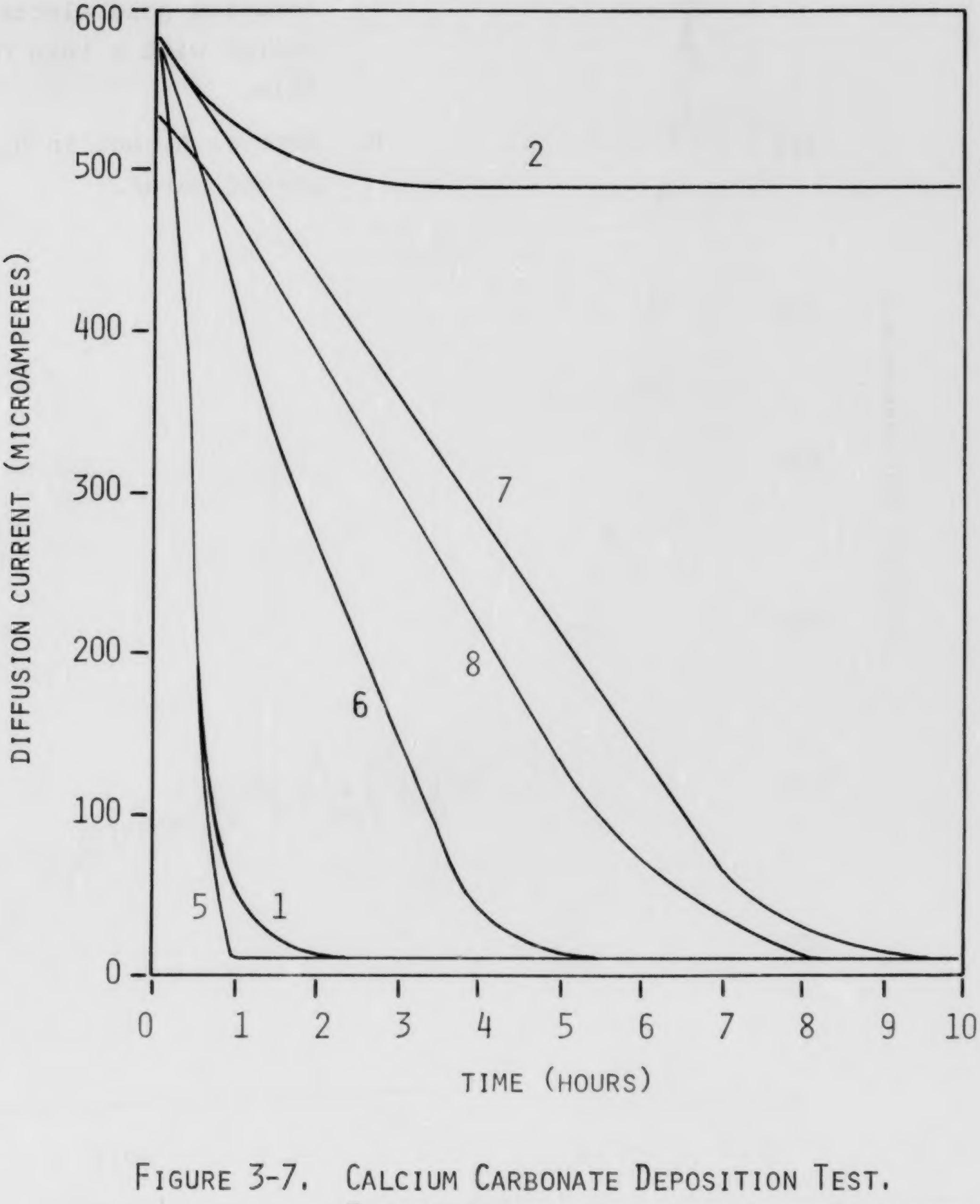


FIGURE 3-7. CALCIUM CARBONATE DEPOSITION TEST. EFFECT OF INITIAL SOLUTION COMPOSITION ON RATE OF FILM FORMATION

TABLE 3-IV

SUMMARY OF DATA FROM ANALYSES OF TEST SOLUTIONS

CURVE IDENTIFICATION (FIG.2)	HARDNESS (MG/L AS C_ACO_3)	CALCIUM (MG/L)	TOTAL ALKALINITY (MG/L AS C_ACO_3)	SOLUTION PH MEAS	LANGELIER PHS	LANGELIER SATURATION INDEX	RYZNER STABILITY INDEX	DIFFUSION CURRENT SLOPE (μAMPS/MINUTE)
1	221	88.5	59.0	8.22	7.60	+0.65	6.92	10.08
2	230	92.0	14.5	7.56	8.16	-0.60	8.76	0.87
5	174	69.5	65.0	8.31	7.63	+0.68	6.95	11.32
6	192	77.0	34.4	8.03	7.86	+0.17	7.70	2.25
7	88	35.2	40.4	8.08	8.14	-0.06	8.20	1.24
8	123	49.2	35.2	7.92	8.05	-0.13	8.18	1.43

Mathematical analyses of solutions 6, 7 and 8 are not conclusive with respect to scale formation, but the CCDT has shown conclusively that a scale can be formed from these solutions.

The question of whether or not a water is sufficiently scale forming to deposit a protective film at an iron pipe is still to be explored. All of these experiments have been performed in synthetic solutions or known composition. None of the test solutions in Fig. 3-7 contained any constituent which might have accelerated or inhibited the deposition of calcium carbonate. It is, therefore, possible to equate the results of the CCDT with mathematical analysis of the solutions. The slope of the diffusion current decay curve should show a correlation with the Langelier and Ryzner indices. Figures 3-8 and 3-9 are such plots of log (CCDT Slope) vs. the Langelier Saturation Index and the Ryzner Stability Index, respectively.

This interpretation of CCDT data provides information of interest to the water works industry. If the CCDT is to be useful to a water works operator, it must provide an easy-to-use index against which he can compare his treatment process. Correlation with the Langelier and Ryzner indices is particularly important. The theoretical indices do not take into account the effects of accelerating or inhibiting constituents in the water. The CCDT does.

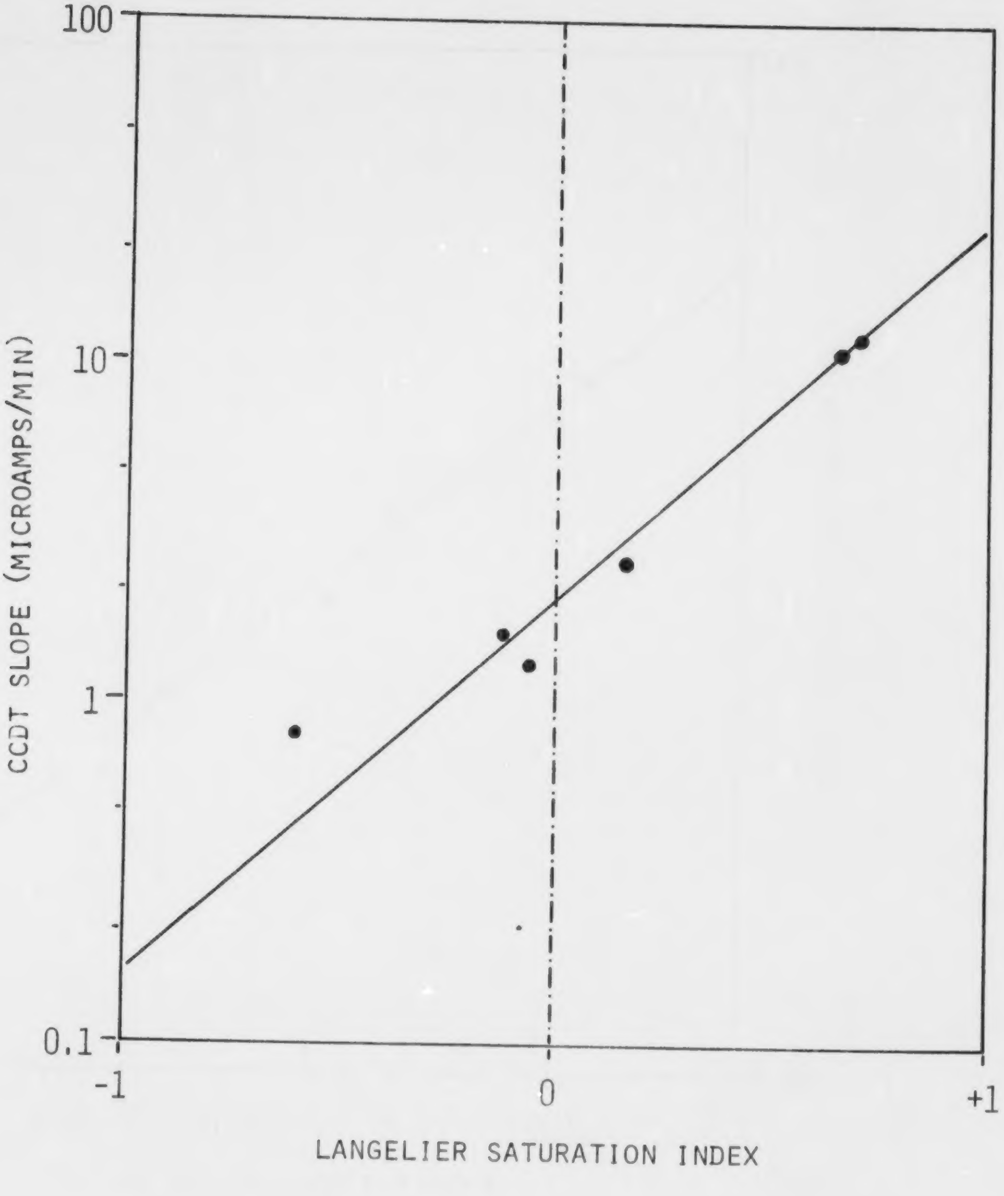


Figure 3-8. Correlation of CCDT slope with Langelier Saturation Index

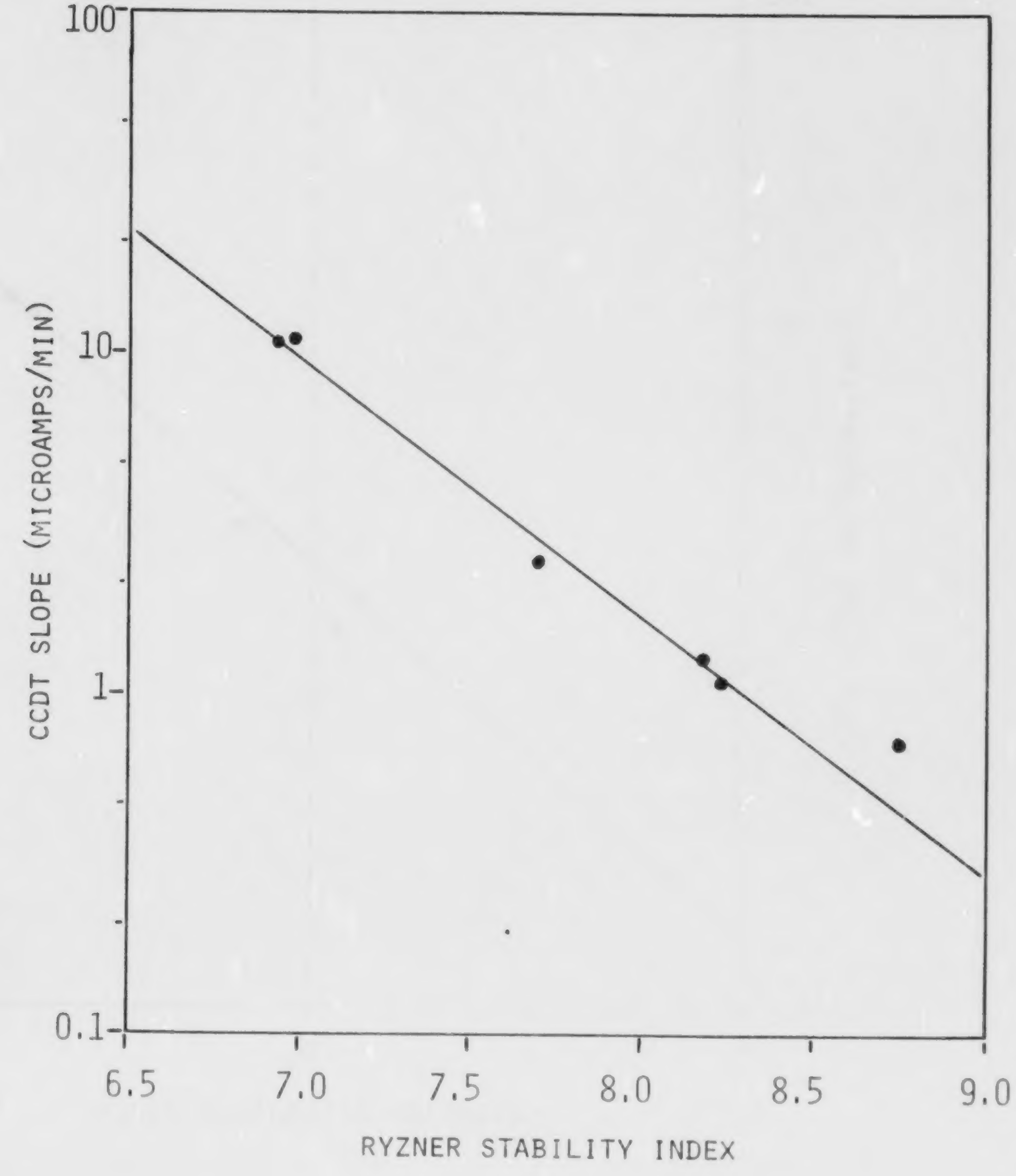


FIGURE 3-9. CORRELATION OF CCDT SLOPE WITH RYZNER STABILITY INDEX

The proposed CCDT method for electrochemical measurement of $CaCO_3$ stability offers the following advantages over currently available techniques:

1. It is a short term test which does not require a great deal of operator attention, and as such, may be applicable as a semi-continuous technique.
2. It indicates the actual amount of $CaCO_3$ being deposited by a given water.
3. It may be used to characterize the rate of dissolution or deposition of $CaCO_3$ films by following changes in the diffusion current with time.
4. It may be used to characterize the structure of $CaCO_3$ film deposited, by measuring its permeability coefficient to dissolved molecular oxygen. This has been related to $CaCO_3$ crystallinity in earlier work reported by McClanahan[20] and Mancy.[19]

3.4 SUMMARY

Methods of characterizing the calcium carbonate saturation equilibrium or "stability" of a water as it relates to the reversible pipe scaling process and inhibition of corrosion of iron water distribution mains were explored in detail. Methods of evaluating this parameter continuously by measuring pH and hardness changes in waters which have been subjected to contact with marble chips or powdered calcium carbonate were rejected because of the long contact period required for reaching saturation equilibrium. A new method which does not require the achievement of saturation equilibrium for characterizing stability is being studied. This method, the Calcium Carbonate Deposition Test, utilizes a rotating inert electrode. It is rapid and provides more information than any of the classical techniques - information about the quality, thickness and rate of deposition of the calcium carbonate film. It also functions without interference from constituents in the water which may accelerate or inhibit the deposition process. The CCDT, although significantly different from previous tests, can provide an index number similar to those which have been used for many years in the water works industry.

4.0 CHARACTERIZATION OF TRACE METALS IN DRINKING WATER BY ANODIC STRIPPING VOLTAMMETRY

4.1 GENERAL

There is growing national concern for the safety of community water supplies. Of particular concern are the long term toxic effects of trace metal contaminants which are not removed by conventional water purification processes - e.g., Cu, Pb, Cd, and Zn, present in the nanogram to microgram per liter ranges.

It is known that trace metals are necessary constituents in many metabolic processes. Such metals as Cu, Pb, Cd, Co, Zn, and Mo have been found in the body in trace amounts, although the functions of some of these metals are not known. It is generally accepted that excessive amounts of these trace elements interfere with certain biochemical processes and exert toxic effects. Although normal daily metal intake is not excessive, the body has the capacity to concentrate some of these metals by an accumulative storing effect.

Most surface water supplies have characteristic trace metal content that can be related to a geochemical origin. Higher levels can be traced to air-borne or water-borne pollution. Underground supplies have different trace metal content, characteristic of the underground geological formation. In addition to the water source, metals may be introduced as impurities in chemicals added to the water during the treatment process, or as a result of corrosion in municipal distribution systems and individual homes.

Data on the levels of trace metals in drinking water supplies are scarce, primarily because simple analytical procedures capable of detecting and measuring them have not been readily available. Except for activation analysis and anodic stripping voltammetry, direct measurement of trace metals cannot be made without concentration of the test solution, i.e., separation, digestion with acid and concentration, which frequently modifies the physicochemical characteristics of the species under investigation.

Although activation analysis offers the high sensitivity required for trace analysis, its use is limited by the availability of reactor facilities. Further, it is an elemental analysis procedure that provides no information about oxidation state or degree and type of complexation.

The analytical feasibility of anodic stripping voltammetry (ASV) for trace metal analysis in natural and waste waters has been established.[29] In addition to its high sensitivity, simplicity and portability, ASV has the unique capability of characterizing free versus complexed trace metals, and is amenable to automation for continuous monitoring applications.

4.2 THEORY

ASV consists of: (1) a pre-concentration (pre-electrolysis, cathodic deposition or plating) step, in which the metal ion (or ions) of interest is reduced by controlled potential electrolysis and deposited as an amalgam on the surface of a composite mercury graphite electrode (CMGE), and (2) anodic dissolution (reverse electrolysis or stripping), in which the metal is oxidized and returned to solution. ASV is, therefore, a nondestructive method of analysis.

The concentration or plating step is carried out under reproducible conditions so that concentration onto the electrode is quantitative (total plating), or a reproducible fraction of the desired component is deposited from solution (partial plating). By controlling the potential during this process, the more easily electrolyzed constituents can be separated. Thus, the concentration process is performed by applying to the electrodes a potential which is cathodic of the polarographic half-wave potential by approximately 0.3 to 0.4 volts (where the current has its limiting value), and maintaining this potential for a given period of time under the reproducible conditions of stirring, type and area of the microelectrode, and composition of the medium. After a short rest period (which allows the solution to become quiescent), the stripping process is initiated.

The stripping process is performed by a voltammetric scanning procedure which produces a response proportional to the amount of material deposited. The resulting "stripping voltammogram" produces peaks, the heights of which are proportional to the concentrations of corresponding electroactive metal ions, and the potentials, a qualitative indication of the nature of the species present in the solution. Thus, the important characteristics of the voltammogram are: the heights of the peaks (peak current, i_p, in microamperes), peak height at 1/2 i_p (W 1/2 in volts or millivolts), and peak potential (E_p, in volts). These characteristics are affected by the type of microelectrode used, and by the rate of voltage change (sweep rate, ν, millivolts per second) employed in the stripping process.

The peak value of the current is proportional to the concentration of the reduced species, the area and thickness of the electrode, and the potential scan rate, as shown in Equation (4.1):

$$i_p = (ZFAl\frac{\phi}{e}\nu)\ C_R \qquad (4.1)$$

where:

i_p = peak current

Z = number of electrons transferred

F = the Faraday

A = electrode surface area

l = thickness of mercury film

$\phi = \frac{ZF}{RT}$

ν = potential scan rate

e = Naperian logarithm

C_R = concentration of reduced species

Film thickness is determined by controlled electrolysis of the mercury onto a graphite electrode. The value of i_p varies nearly proportionally to the scan rate for very thin mercury films; however, it varies a great deal with film thickness at higher sweep rates. For lower values of 1, i_p varies only slightly with film thickness.

Equation (4.2) depicts peak position:

$$E_p = E_o + \frac{e}{\phi} \log \frac{\delta l \nu \phi}{D} \qquad (4.2)$$

where:

E_p = peak potential

δ = Nernst diffusion layer

D = diffusion constant

E_o = standard potential

E_p, then, is a function of scan rate, film thickness, and the Nernst diffusion layer. This theory does not hold for fast scan rates with very thick films. Peak width, which is important in resolution, varies only slightly with scan rate when the mercury thickness is small, and varies slightly with thickness with a slow scan rate.

A typical ASV voltammogram, shown in Fig. 4-1, demonstrates the resolution that permits selective analysis for elements with a high degree of sensitivity. Standard

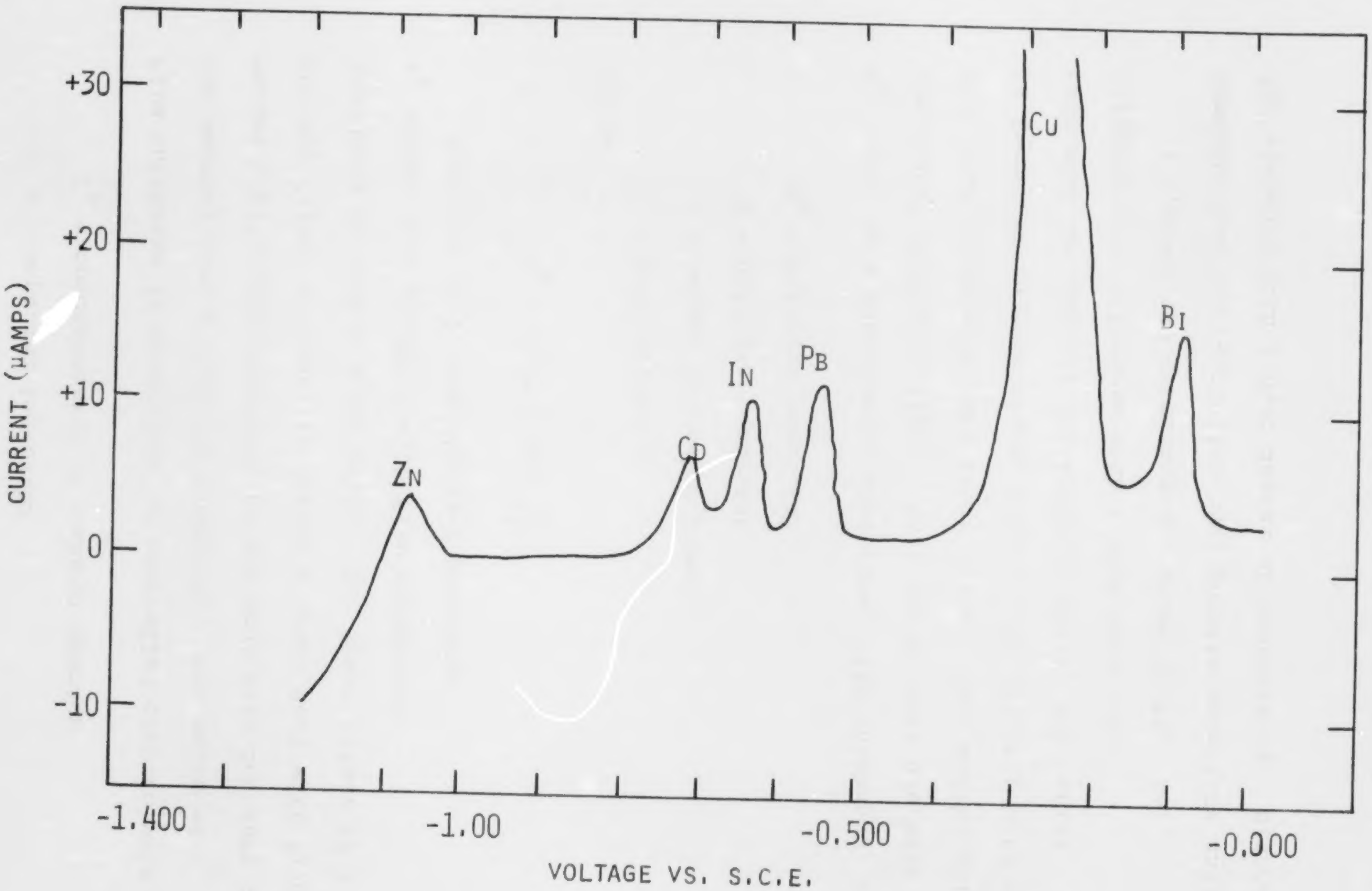


FIGURE 4-1. TYPICAL ASV VOLTAMMOGRAM

additions with the sample concentration in the range of 1 to 3 x 10^{-8}M for each metal except for copper, which was 1.7 x 10^{-7}M, were used in obtaining this voltammogram. The electrodeposition time was 5 minutes at -1.35v versus S.C.E. The sample volume was 10 ml and pH, 5.5 - 6.0. A combination of acetic acid, acetate, and sodium chloride made up the supporting electrolyte.

4.3 EXPERIMENTAL

4.31 MATERIALS AND METHODS

The equipment shown schematically in Fig. 4-2 was used for the analyses. A Heath amplifier model #EUW-19-B equipped with a polarographic module #EUA-19-2 and a chopper stabilizer #EUA-19-4 was used to scan the voltage of one cell during the dissolution step. The current was charted on an Esterline Angus Chart Drive Recorder #227 during the early phases of the investigation. Later, a Heath recorder #EUW-20-A was substituted. A VTVM #EUW-24 was also used.

To increase the efficiency of the analysis, a multiple cell unit was utilized. A second Heath amplifier regulated the potential of 4 cells during the electrodeposition. A switching module consisting of a 3 stack switch with shorting contacts on the reference and counter electrodes and a non-shorting contact on the mercury-graphite electrode was used to transfer the cell to the polarographic module for stripping.

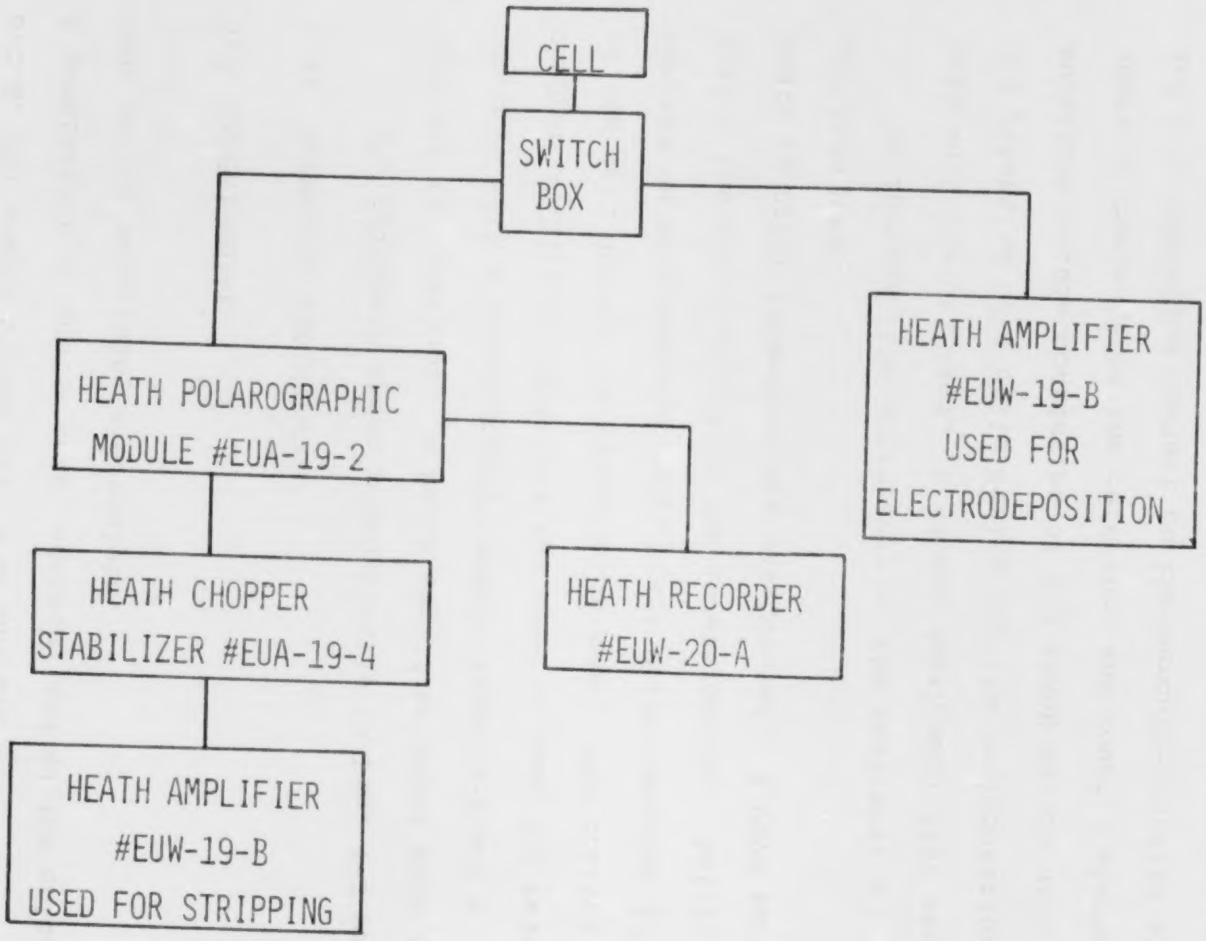

CELL
SWITCH BOX
HEATH POLAROGRAPHIC MODULE #EUA-19-2
HEATH CHOPPER STABILIZER #EUA-19-4
HEATH AMPLIFIER #EUW-19-B USED FOR STRIPPING
HEATH RECORDER #EUW-20-A
HEATH AMPLIFIER #EUW-19-B USED FOR ELECTRODEPOSITION

FIGURE 4-2. SCHEMATIC ILLUSTRATION OF ASV EQUIPMENT

The cell, shown schematically in Fig. 4-3, consisted of a quartz vial, to minimize metal adsorption, with three electrodes. Nitrogen for deaeration and constant stirring was bubbled through a teflon tube with a platinum wire inserted inside for rigidity.

The test electrode was a composite graphite mercury electrode, a spectrographic grade graphite rod impregnated under vacuum with paraffin to fill all porous channels in the graphite. Outer paraffin coatings were applied and the electrode tip was polished to a smooth, nonporous surface. Mercury was plated onto the exposed graphite at -0.4v versus a Ag/AgCl electrode. The reference electrode was a Ag/AgCl couple. A platinum counter electrode was immersed in 0.1M NaCl electrolyte. These two electrodes had porous vycor tips, permitting electrical contact to occur with the sample solution.

Nalgene sample bottles, 125 ml, were pretreated to avoid adsorption of metals from the walls, by digesting 100 ml of laboratory tap water at 65°C. for 4 hours with 0.2 ml $HClO_4$. The detectable metal concentration was significantly improved by the acid addition, providing H^+ competition to replace the metal from its chelated form. The acid addition also lowered the pH to 2 and kept the metal from being hydroxylated. Digestion was necessary to increase the kinetics for metal replacement, and perhaps to facilitate ligand breakdown. The samples were cooled

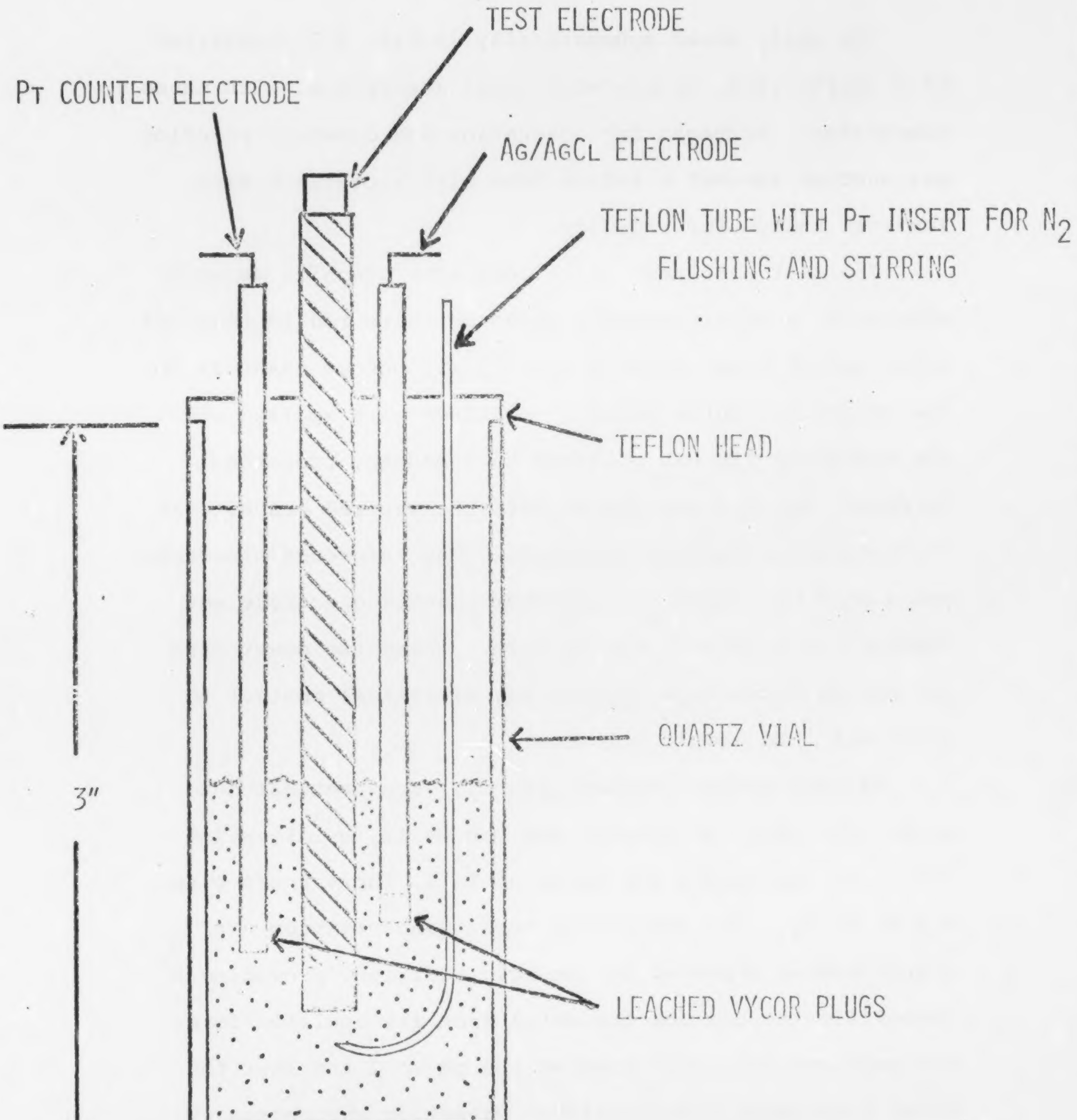


FIGURE 4-3. ANODIC STRIPPING VOLTAMMETRIC CELL

to 23°C. before analysis. Each water sample was run in four cells simultaneously, and rerun with an internal standard. The period of electrodeposition was 30 minutes. A rest period of approximately 5 seconds occurred between the time the stirring was stopped and the stripping began. Scan rate was 2 volts per minute. Samples were analyzed on the day of - or day after - collection. At any later time, the metal content was significantly different. The perchloric acid added a constant amount of contamination of 0.42 ppb Pb and 0.44 ppb Cu.

A test program was developed to determine the feasibility of anodic stripping voltammetry for measuring trace metals in municipal water supplies. Samples were taken from the distribution system at various locations along a continuous transfer main in the city of Ann Arbor. Because it was impossible to tap the main directly, locations such as university buildings, motels, and gas stations were selected as sampling sites. The water was allowed to run a minimum of 10 minutes before collection. The sampling route was selected with assistance from the staff of the Ann Arbor Water Department so there were no contributions from interconnecting mains.

Diurnal monitoring was attempted by grab sampling water flowing continuously from the same tap for 14 hours. The sample tap was located in the School of Public Health, University of Michigan, and sampling occurred both week days, when water consumption was great, and weekends, when usage was low. Samples were collected every 2 hours.

4.32 RESULTS AND DISCUSSION

Fig. 4-4 is a representative plot of diurnal variations detected during week days in the month of May. Lead variations are insignificant. The high initial concentration is attributed to stagnant water in the tap at the time of the first sampling. This water was in the building pipes overnight, allowing more lead to desorb from the pipe. It is assumed that water consumption during the night was low, since the University dormatories in the vicinity were unoccupied. The copper concentration shows a greater degree of variation. This is attributed to copper piping in the building. Again, note the higher concentration of copper in the stagnant water. After 6 A.M. the water was allowed to run continuously. Throughout the entire investigation, the Cd concentration was too low to be detected by this technique. The final rise in both lead and copper is also attributed to less usage.

Daily variations were detected during May when the lead and copper levels dropped to 0.6 to 0.8 ppb and showed variations typical of those in Fig. 4-4.

Results of diurnal monitoring during the late summer are shown in Fig. 4-5. Variations are attributed to the surface and ground water source of Ann Arbor's water supply. During late summer the water level is low,

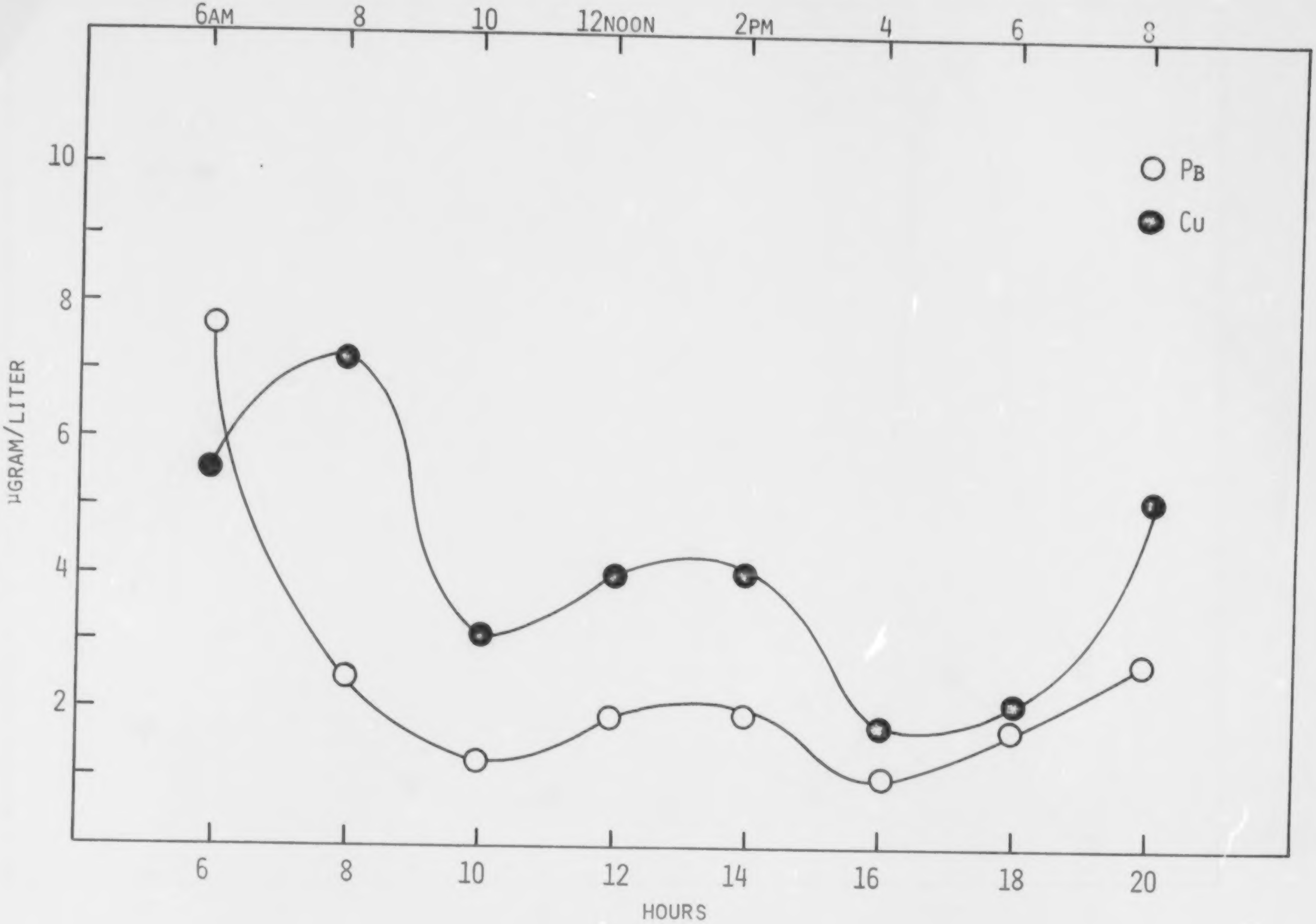


Figure 4-4. Diurnal variations of Pb and Cu in early summer

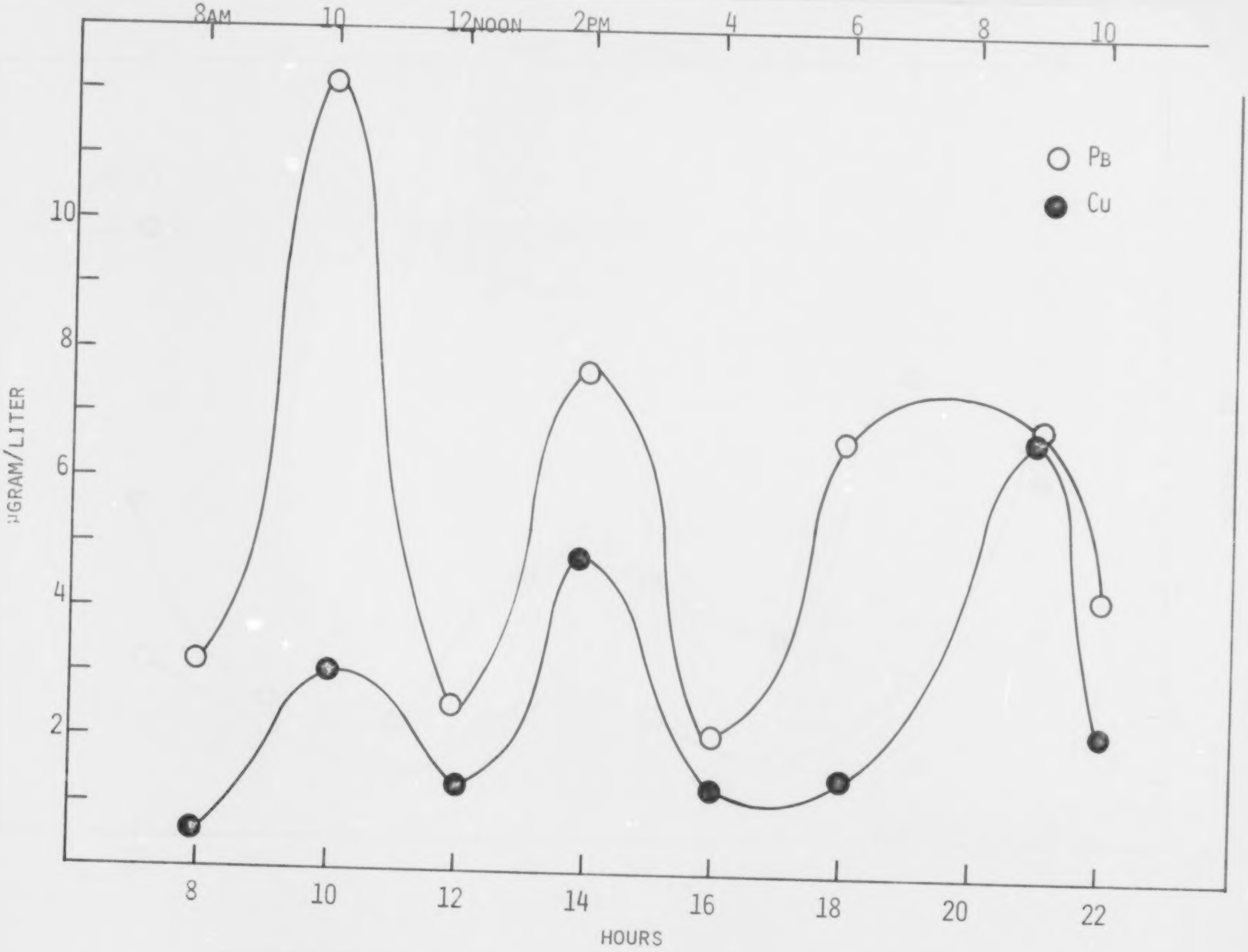


FIGURE 4-5. DIURNAL VARIATIONS OF Pb AND Cu IN LATE SUMMER

concentrating the metals to a greater extent. Because lower Michigan had a relatively dry summer, the water consumption increased from the spring level. This, combined with meal time water usage on a weekend, contributes to a greater variation in the metal content.

Sampling points on the transfer main used in this study are shown in Fig. 4-6. The sample pathway started at the purification plant with a 14 inch main. This connects to a 12 inch transfer main, then to a 10 inch pipe and finally a 6 inch pipe near the university buildings. Transfer mains in Ann Arbor are generally of ductile iron lined with concrete, with cast iron gates. This particular main may have been cast iron only. All building piping is made of copper.

4.4 SUMMARY

Thin layer anodic stripping voltammetry is a practical method to use for characterizing trace elements in municipal water supplies. It measures both free and complexed forms without preconcentration procedures. Using this method, trace metals in water supplies can be measured with ease, with a high degree of sensitivity and selectivity. Cost of the apparatus is comparatively low, and it can be adapted for *in situ* use.

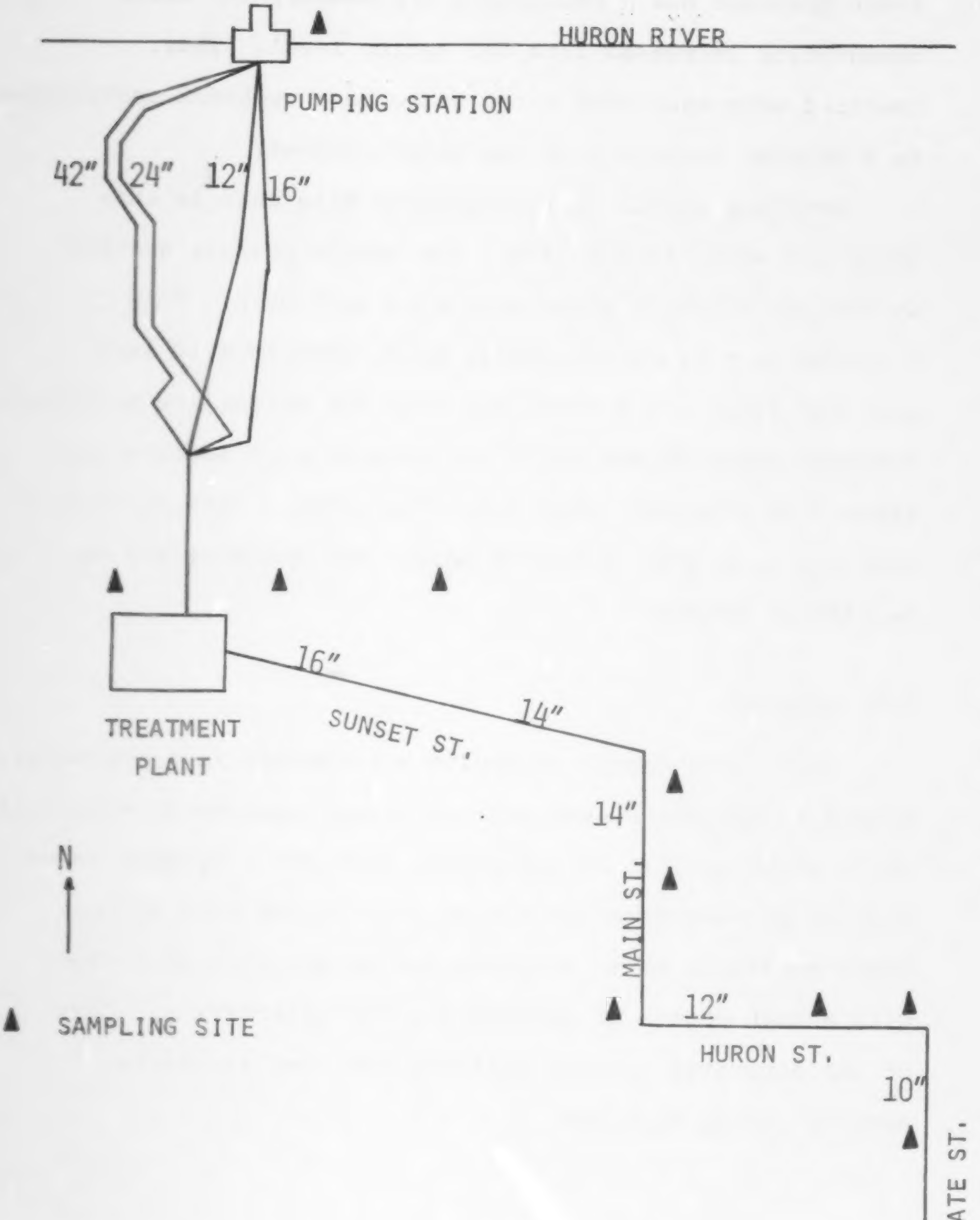


FIGURE 4-6. DISTRIBUTION SYSTEM MAP
SHOWING SAMPLING SITES

5.0 GROSS ORGANICS

5.1 GENERAL

Knowledge of the trace organic content of processed waters is important for aesthetic as well as health reasons. Organics that escape the water treatment process may vary quantitatively and qualitatively in each water supply. This variation may be daily or seasonal, depending on the nature, location and uses of the source. Failure to completely remove organics from a finished water may result from operating practice at the treatment plant or the need for additional treatment facilities. Thus, in order to evaluate the effectiveness of a water treatment process, the level of organic materials present in the source of supply and the finished water is necessary.

Until recently, most methods used for measuring total organics could be operated only on a batch basis. Adaptation of these methods to continuous monitoring is either not possible technologically or economically impractical.

Relative amounts of trace organics can be measured by considering the physical properties of a group of organic compounds, some of which are always found in natural waters as a result of biological activity, and some of which are present as a result of industrial activity. Among such compounds are the nucleic acids and nucleic-acid-containing compounds, proteins, phenols and commercial solvents. These compounds possess aromatic or conjugated molecular configurations that can absorb electromagnetic radiation in the upper ultraviolet range (200-300 nm) due to their electron mobility. Continuous measurement of UV absorption is simple and relatively low in cost. The potential value of UV measurement of gross organics has prompted the production of several commercial instruments specifically designed for continuous monitoring. The feasibility of using this technique for potable water monitoring applications has been studied, and one of the commercially available systems, the Aqua Test Water Quality Monitor, evaluated with respect to its operational requirements and data interpretation. UV absorbance data were compared with total organic carbon (TOC) measurements on samples of processed water.

5.2 THEORY

UV absorbance monitors operate on the principle that organic compounds with aromatic or conjugated bonding configurations absorb UV light in the range of 200-300 nm. For operation on a continuous basis, a UV scan in the upper UV range is not possible, therefore, the monitor is preset at some known wavelength. The Aqua Test monitor is set at 253.7 nm which is the wavelength of light emitted by a low pressure mercury vapor lamp. The use of a preset wavelength results in quantitative and qualitative losses and causes a large share of the problems associated with the instrument. At a single UV wavelength of 253.7 nm, not all organics will absorb completely or even at all, while some inorganics will absorb partially and cause artifically inflated readings. UV light of this wavelength is useful for aromatics or other conjugated compounds, but pure aliphatics which are related to taste and odor or health problems may not register in the absorbance reading.

Inorganics, chlorine, for example, partially absorb at 253.7 nm, thus the UV monitor can be calibrated in standard solutions of chlorine. Effects of physical interferences - turbidity, air bubbles, and bacteriological films - must also be considered in interpreting UV data.

5.3 EXPERIMENTAL

5.31 MATERIALS AND METHODS

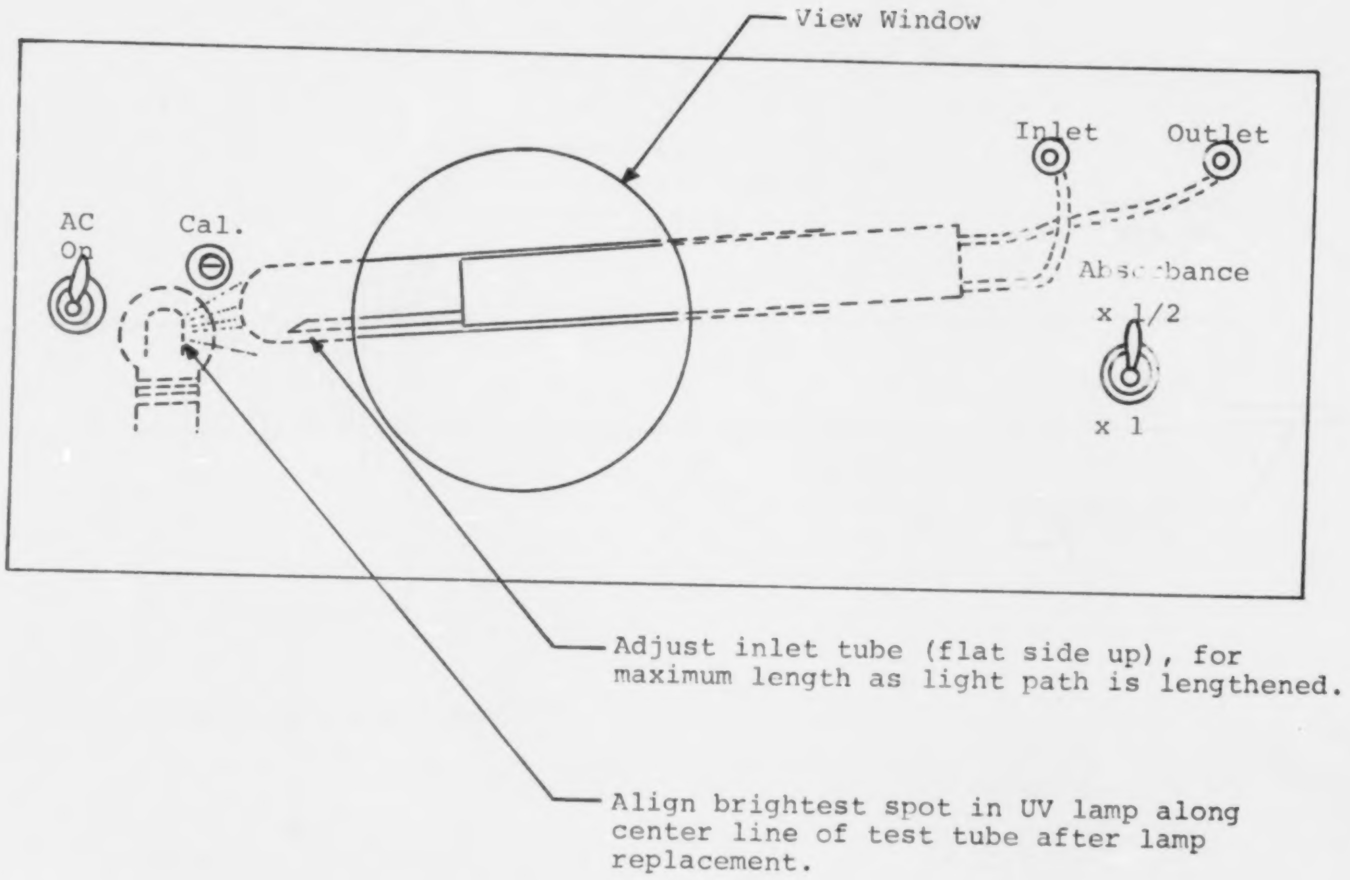
TOC determinations were made with a Beckman Carbonaceous Analyzer. Standard TOC solutions were made with inorganic carbon-free water and glucose. Inorganic carbon was removed from samples and standards by lowering the pH to 1.0 with HCl and bubbling with purified nitrogen.

UV absorption scans were made with a Bausch and Lomb 505 spectrophotometer and a cell of 10 cm path length. The instrument was zeroed with organic-free distilled water prepared by redistillation from boiling permanganate solution. Tap water samples were collected from distribution systems in the following Michigan communities: Petersburg, Manchester, Chelsea, Belleville, Ypsilanti and Ann Arbor. In addition, two well waters designated as X and Z were sampled in the same manner. These waters were monitored for UV absorption and TOC over a one month period.

The Aqua Test Monitor was used to measure UV absorbance at 253.7 nm. In this instrument, a low pressure mercury lamp provides the essentially monochromatic UV light. Voltage outputs of sample and reference UV detectors are electronically processed to display the logarithm of their ratio on an accompanying strip chart recorder. Fig. 5-1 shows a schematic front view of the flow assembly, and Fig. 5-2, the detector assembly. (Figs. 5-1 and 5-2 are reproduced with permission of the Aqua Test Corporation, Ames, Iowa.) The detector assembly, which contains flow lines and the sample UV detector, is adjustable to provide a 2 to 14 cm path length. Chlorine standards were prepared from commercially available Chlorox bleach, and phenol standards, from Analytical Reagent grade chemicals, both in redistilled water. A percolation debubbler was also provided by Aqua Test Corporation.

5.32 RESULTS AND DISCUSSION

Fig. 5-3 shows typical scans in the UV range of processed waters obtained from the sources indicated. Significant differences in the profile of these scans are apparent. All, however, show considerable absorption at a broad range of UV wavelengths.



Adjust inlet tube (flat side up), for maximum length as light path is lengthened.

Align brightest spot in UV lamp along center line of test tube after lamp replacement.

Figure 5-1. Schematic illustration of Aqua Test Monitor control panel[30]

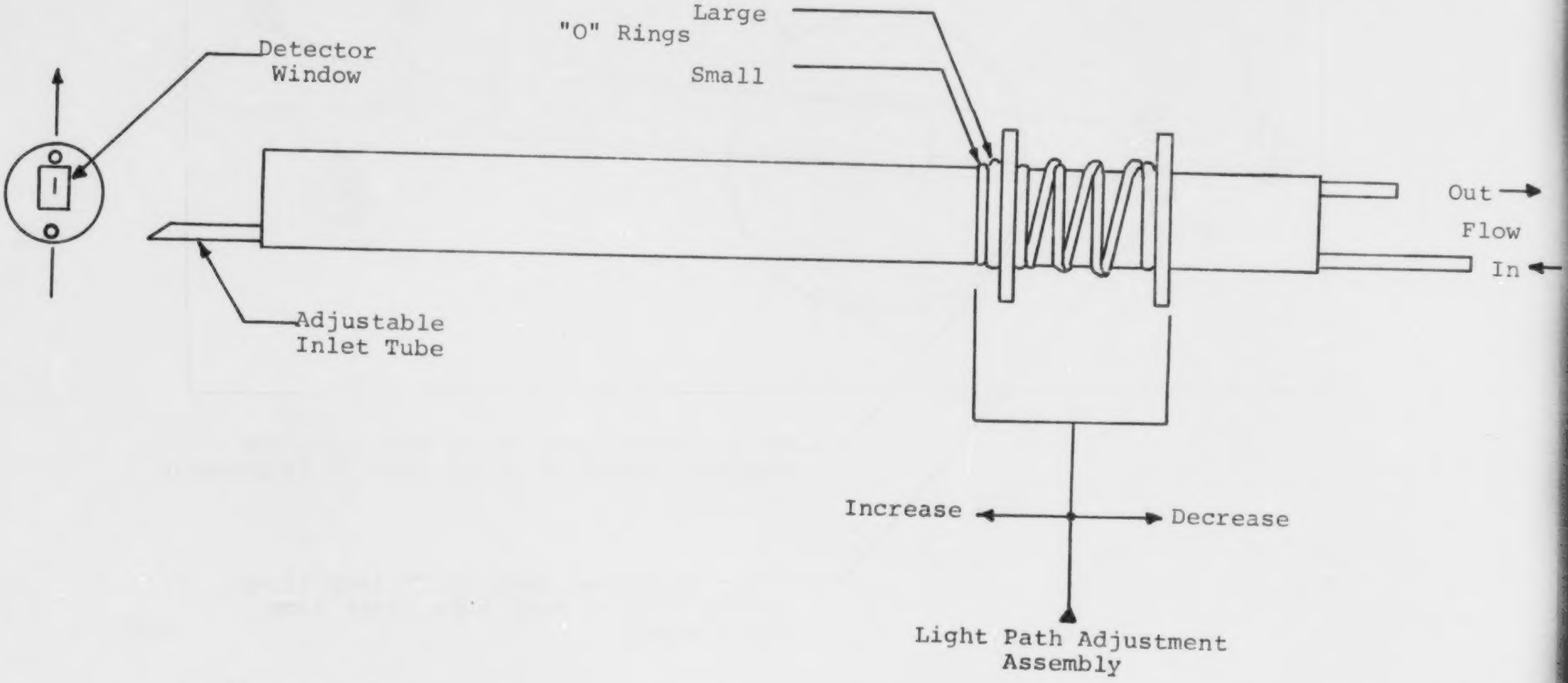


Figure 5-2. Schematic illustration of Aqua Test Monitor detector assembly[30]

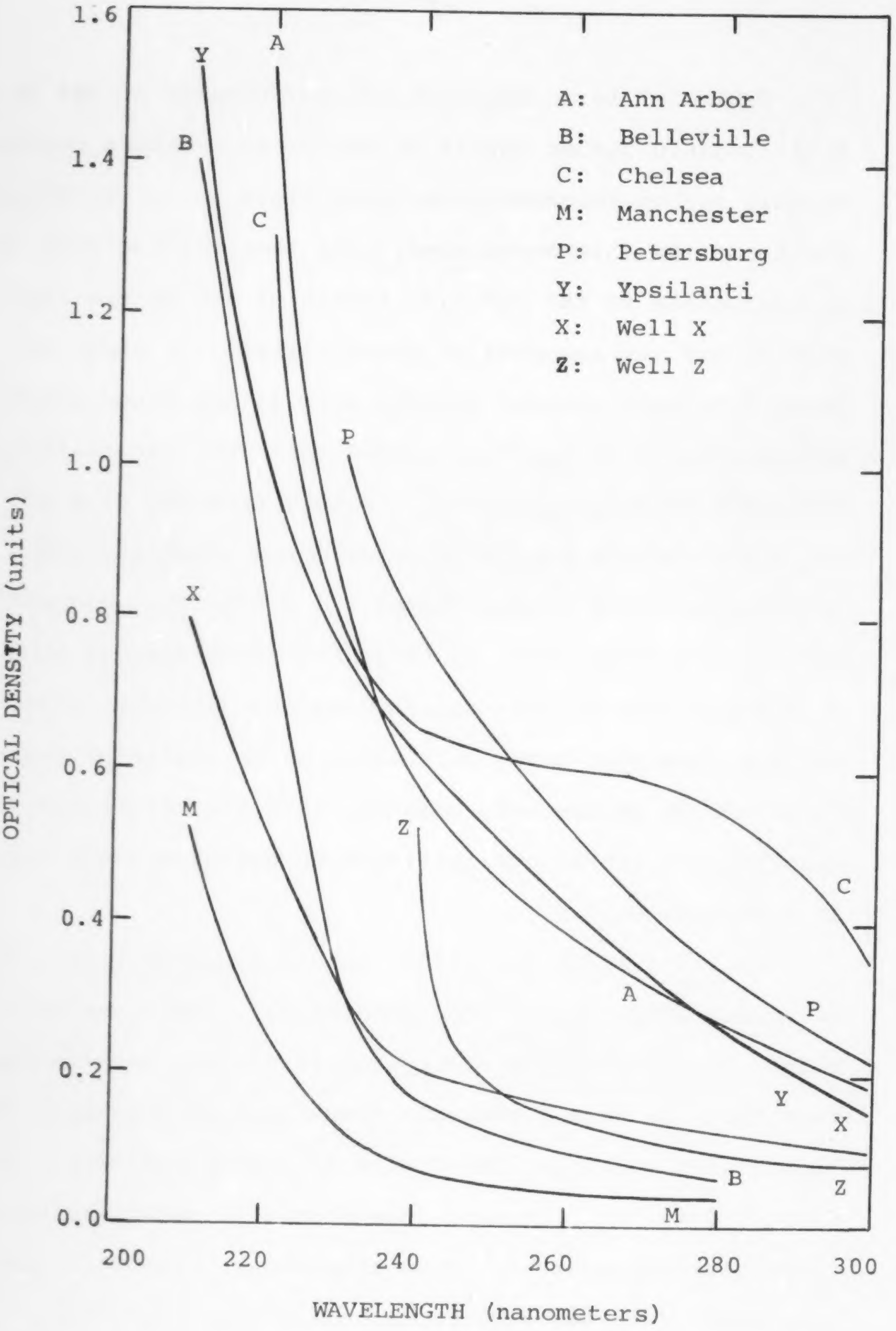


Figure 5-3. UV scans of various processed waters

Table 5-I is a comparison of absorbances at 260 nm with total organic carbon levels of the various waters tested. Organic carbon concentrations were close to the detection limits of the instrument used, thus they are included as an indication of the relative levels of TOC in the test waters, but the accuracy is questionable. As shown in Table 5-I, each optical density unit in Ann Arbor water was equivalent to approximately 8 mg/l TOC. In Belleville, this relationship was 1:17.5. Waters from the City of Ann Arbor and the City of Ypsilanti had about the same UV absorbance:TOC ratio. These two cities are adjacent and use the Huron River as their raw water source; thus it appears that UV data obtained in one city may relate to another, provided both use similar water treatment techniques. It should be emphasized, however, that the material(s) being absorbed may not be qualitatively or quantitatively similar in both cities.

Fig. 5-4 shows the effect on the UV absorption profile of phenol added to one processed water. There was only slight increase in the absorption at 270 nm, despite the fact that the phenol concentrations used were several times higher than the tolerance limits for taste and odor. In Figs. 5-3 and 5-4, organic free distilled water was used to zero the instrument. Thus everything present in the processed water was uncorrected, including inorganic compounds such as nitrates and chlorine. Such compounds absorb strongly in the lower UV range and produce end-absorption

TABLE 5-I

UV ABSORBANCES AND TOC DETERMINATIONS FOR VARIOUS PROCESSED WATERS

Source	Absorbance at 260 nm, units	Organic Carbon, mg/l	Organic Carbon Absorbance
Ann Arbor	0.398	3.3	8.29
Belleville	0.097	1.7	17.53
Chelsea	0.602	2.5	4.15
Manchester	0.056	1.2	21.43
Petersburg	0.523	5.0	9.56
Ypsilanti	0.420	3.3	7.86
Well X	0.143	0.7	4.90
Well Z	0.115	1.2	10.43

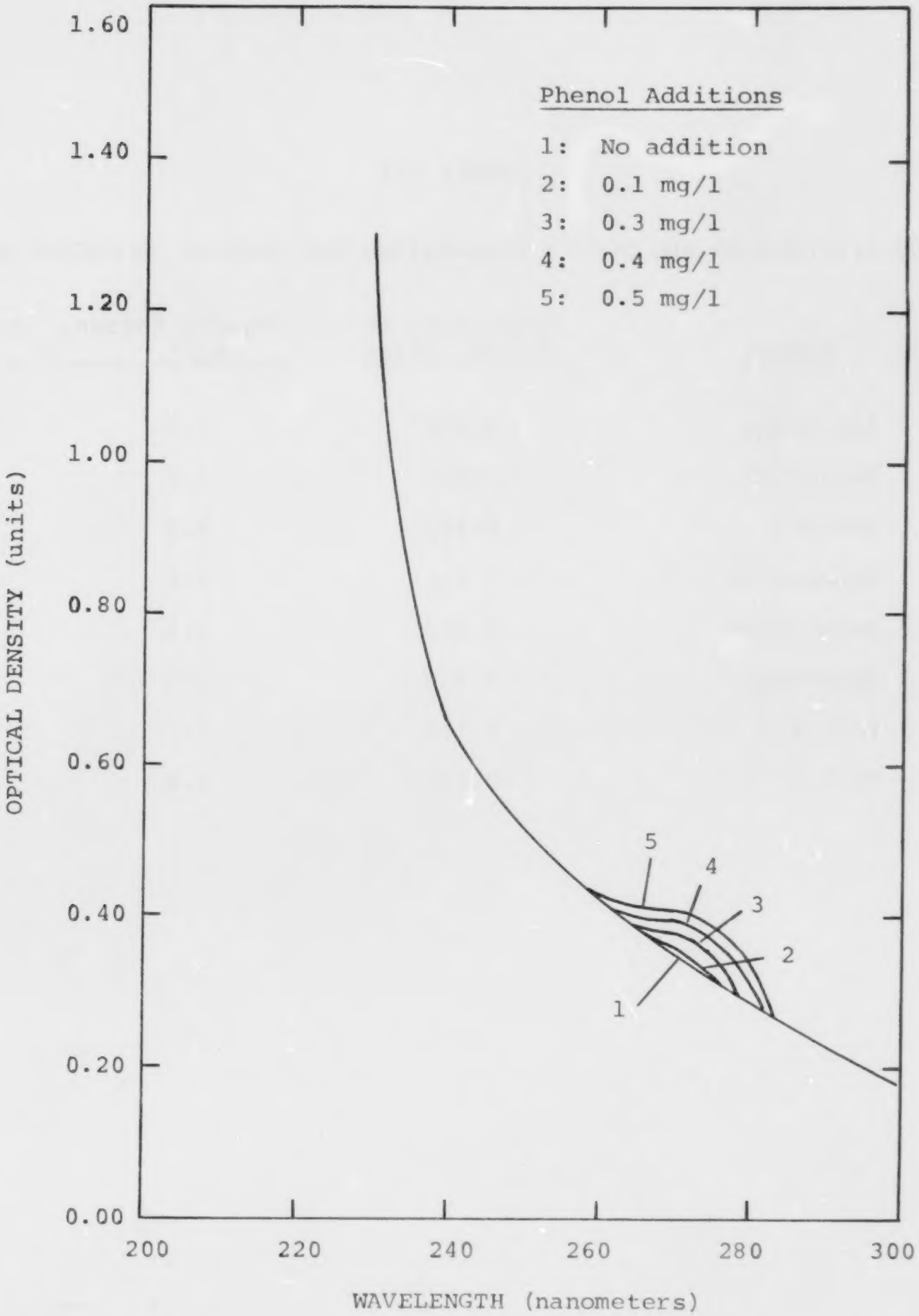


Figure 5-4. UV scans of one processed water with varying phenol additions

which can mask the species of interest. The effect of added phenol on the UV scans in Fig. 5-4 would be seen much more dramatically had the instrument been calibrated with a "standard processed water." Table 5-II lists the absorption values at 260 nm of processed waters over a week's period. Differences in total organic carbon content from day to day for each source were not detected by the carbon analyzer and were essentially the same as those shown in Table 5-I. Variations in UV absorbance data may not be significant because no "standard processed water" was available for standardizing the instrument. Masking and end-absorption by optically active but qualitatively unimportant components could be responsible for variations observed. Calibration of a UV monitor with a standard processed water can eliminate many of the interferences associated with UV monitoring.

Many UV absorbing species show a shift in peak absorption when the pH of their solutions is shifted. The quantitative shift in the Ann Arbor water is demonstrated in Table 5-III. Because of end-absorption effects described earlier, however, the qualitative shifts (peak absorption shifts) may be difficult to observe.

Interferences which tend to inflate absorbance readings can be divided into two groups: one group is chemical in nature, specifically UV absorbing inorganics; the other is physical, and scatters or blocks UV light. The latter group includes turbidity, air bubbles, and bacteriological films.

TABLE 5-II

TIME SURVEY OF UV ABSORBANCES AT 260 nm OF VARIOUS PROCESSED WATERS

Date	Ann Arbor	Belleville	Manchester	Petersburg	Ypsilanti	Well X	Well Z
1-14-71	0.357	0.244	0.081	-	0.444	0.168	0.155
1-15-71	0.328	0.237	0.027	0.482	0.482	0.194	0.155
1-18-71	0.252	0.252	0.027	0.523	0.398	0.155	0.220
1-20-71	0.284	0.244	0.061	0.495	0.357	0.155	0.220
1-21-71	0.319	0.260	0.056	-	0.319	0.119	-
1-22-71	0.284	0.276	-	0.432	0.337	0.143	0.220

TABLE 5-III

EFFECT OF pH ON UV ABSORPTION OF PROCESSED WATER

pH	Absorbance at 270 nm
2.2	0.310
7.0	0.367
10.2	0.495

Phenol and chlorine concentrations necessary to produce equal absorbance values were shown to be in the ratio of 1:5 (phenol:chlorine). In potable water, a residual chlorine concentration of 1 mg/l would appear as 0.2 mg/l of organics. Although this is not a significant interference at any reasonable organic level, a number of inorganic compounds could combine their partial absorbances to cause a significant error. Nitrate, for example, has an absorbance peak at 206 nm and would register in a manner similar to that of residual chlorine.

Work by Dobbs et al[31] reported 5 cm absorbances for 1 JTU solutions of silica and bentonite to be 0.060 and 0.130 respectively, thus the interference effect of turbidity can be significant. Comparison of continuous turbidity measurements with gross organics levels indicates if particularly large changes in absorbance readings are effects of turbidity.

Under normal operating conditions, interferences from air bubbles are no problem. If the water supply is abnormally cold and under relatively high pressure, bubbles may form; however, flow rate through the monitor is slow enough that temperature equilibration usually occurs before the water reaches the flow cell. Aqua Test recommends no more than 1 meter head of water for best flow conditions,[30] so in general no de-bubbling equipment is necessary. In this study a percolation de-bubbler was tested. This unit percolates air through the sample to allow bubbles to separate before the sample enters the monitor. Over a period of several days, the test stream was alternately run through the de-bubbler and taken directly from the tap. No differences in absorbance readings were observed.

Although the 253.7 nm wavelength of the mercury lamp is in the germicidal region, bacteriological films may form in the flow cell, especially over the sample UV detector at the end of the cell when the organic or turbidity levels are high enough to screen out a large portion of the UV light.[30] This interference can be controlled by periodically zeroing the monitor with distilled water, and mechanical cleaning of the flow and detector assemblies when significant changes in absorbance for distilled water are noted over a period of time.

5.4 SUMMARY

The usefulness of monitoring gross organics with UV light absorbance was demonstrated by comparing UV absorbances and TOC measurements of various community water supplies. The correlation ratio is different for various water supplies, and may not be exactly constant for the same supply; however, it appears that UV absorbance data may be helpful in assessing the overall organic content of processed water. The effect of a number of inorganics on the absorbance measurements can be eliminated by calibrating the instrument with a standard process water.

The Aqua Test UV monitor was evaluated with respect to operational requirements. Effects of turbidity, air bubbles, and bacteriological films were investigated.

Monitoring of organics by UV absorption has the following limitations: (1) only organics containing conjugated bonding configurations are sensed, thus many potentially dangerous or non-aesthetically pleasing compounds may be missed, (2) UV absorbing inorganics like chlorine and nitrate may interfere, and (3) physical agents such as air bubbles, turbidity, and bacteriological films may interfere. Nonetheless, absorbance data can show long term trends and significant changes in organic content which indicate decreased efficiency in organic removal equipment or a cross connection in the water distribution system.

6.0 RESIDUAL CHLORINE

6.1 GENERAL

The importance of maintaining a chlorine residual for purposes of disinfection is well established, and regularly practiced in public water supplies. However, ineffective germicidal action occurs at a low concentration level, and taste and odor problems develop at higher levels; thus, approximately 1 mg/l should be maintained. For these reasons, it is desirable to include instrumentation in the proposed Water Quality Monitor for measuring residual chlorine.

Two methods for measuring residual chlorine were evaluated with respect to feasibility for potable water monitoring applications: (1) a Capital Controls Residual Chlorine Analyzer, and (2) a selective ion electrode method. The Capital Controls Analyzer is a commercially available amperometric device in which chlorine acts as an electrolyte in a gold-copper cell, and current output is calibrated in terms of chlorine content. The selective ion electrode method, developed as a batch technique by Orion Research, Inc.,[32] involves the quantitative reaction of chlorine with iodide ion, (I^-) and measurement of the loss of iodide with an Orion iodide electrode. The change in electrode potential can be calibrated in terms of chlorine in the sample. The first method was studied briefly with respect to accuracy with potable water. The Orion method's accuracy was studied on batch samples and a proposal developed regarding the feasibility of automating this technique.

6.2 THEORY

Capital Controls Analyzer[33]

The Capital Controls Analyzer employs the same basic principle as an amperometric titrator, but the method of chlorine concentration determination differs. In both, the free chlorine (or the iodine formed by the quantitative reaction of I^- and combined chlorine) acts as the electrolyte in a gold-copper cell (Fig. 6-1, reproduced with permission of the Capital Controls Company, Inc.) producing a current measurable with a microammeter. In the amperometric titrator, chlorine is titrated with phenylarsene oxide until no current reduction is observed on the microammeter; the Capital Controls Analyzer calibrates the current output directly in terms of chlorine content. The titrator is inherently more accurate, as are most null-point titrations, but the analyzer has the advantage of operating as a continuous flow system. The Analyzer can measure either free or total residual chlorine, depending on whether I^- is added. Standard procedure[5] calls for free chlorine to be measured at pH = 7 and combined chlorine to be measured at pH = 4. Combined chlorine reacts slowly and non-quantitatively

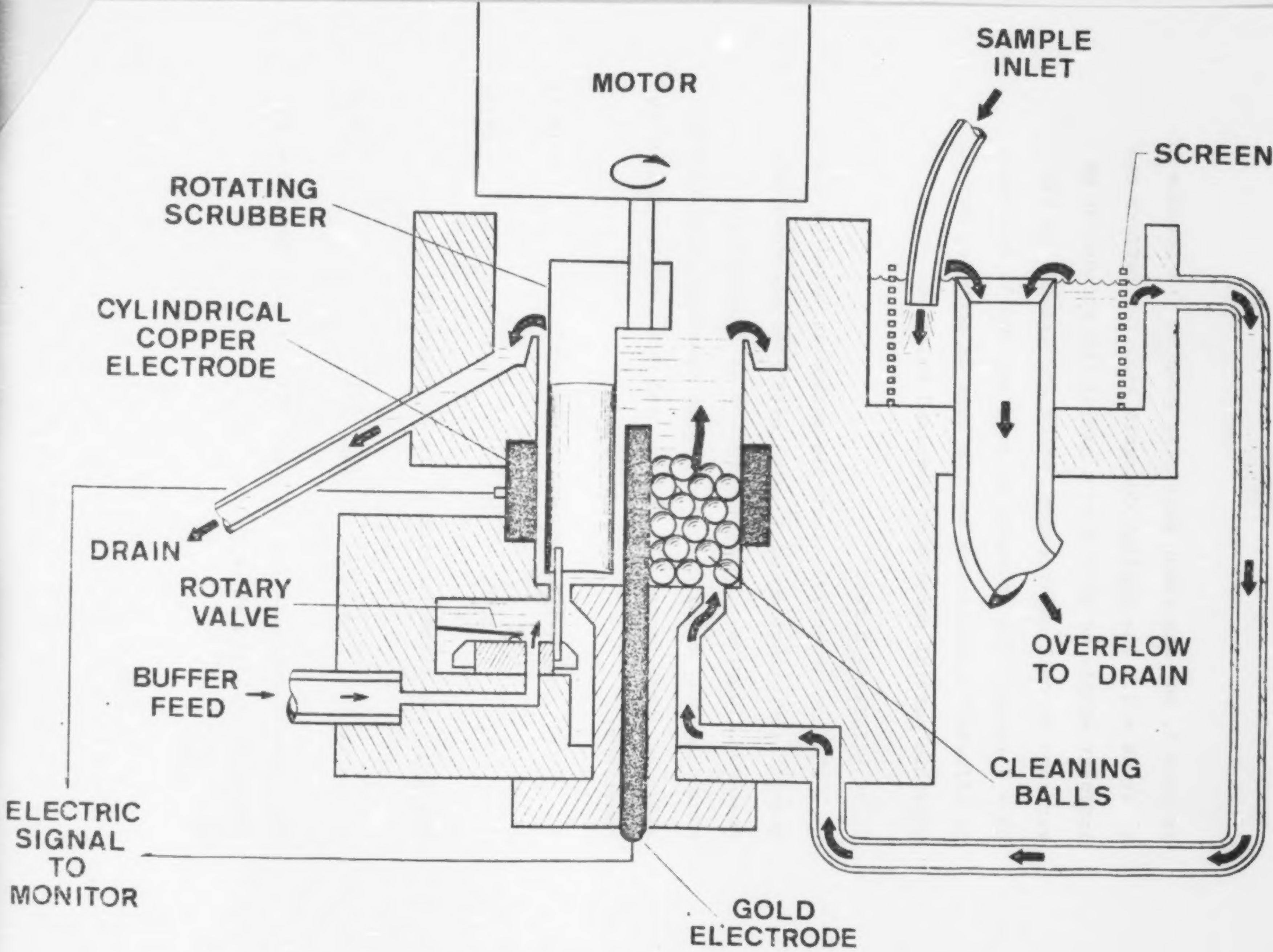


FIGURE 6-1. SCHEMATIC OF CAPITAL CONTROLS RESIDUAL CHLORINE ANALYZER[33]

at pH = 7, but may react partially even in the absence of I^- at pH = 4. The Capital Controls Analyzer buffers the influent sample to pH = 4 to minimize the effects of pH variance on cell calibration, which are greater in the pH = 7 range. The increase in accuracy due to decreased pH effects[34] compensates for the loss in accuracy due to possible partial sensing of combined chlorine.

Orion Electrode Method[32]

The ion selective electrode method is based on the quantitative reaction of I^- with both free and combined residual chlorine. Thus, the method is suitable for measuring only total chlorine. Free residual chlorine can exist in three forms: Cl_2, HOCl, and OCl^-, by the following reactions:[35]

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{6.1}$$

$$HOCl \rightarrow OCl^- + H^+ \tag{6.2}$$

For Cl_2, the reaction with I^- is as follows:

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^- \tag{6.3}$$

The overall reaction for HOCl and OCl^- is also described by Equation (6.3) as shown below:

for HOCl: $$2Cl_2 + 2H_2O \rightarrow 2HOCl + 2H^+ + 2Cl^- \qquad (6.1)$$

$$+ \quad 2HOCl + 2I^- \rightarrow 2OH^- + Cl_2 + I_2 \qquad (6.4)$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^- \qquad (6.3)$$

for OCl^-: $$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (6.1)$$

$$HOCl \rightarrow H^+ + OCl^- \qquad (6.2)$$

$$+ \quad OCl^- + 2I^- + 2H^+ \rightarrow H_2O + I_2 + Cl^- \qquad (6.5)$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^- \qquad (6.3)$$

The reactions for NH_2Cl and $NHCl_2$ chloramines are unknown but various sources report the same quantitativeness as in Equation (6.3).[32] The combined chlorine reaction is quantitative only at pH = 3.5 - 4.5, and the free chlorine reaction is quantitative at all pH levels below 8.0. The total chlorine determination is therefore carried out at pH = 4, using an acetate buffer.

The method consists of measuring the iodide concentration in a reagent solution containing KI, an acetate buffer, and sodium citrate (to eliminate ferric ion reactions with iodide), adding a known amount of reagent to a specific sample volume, and measuring the final iodide concentration. The reagent to sample ratio is 1:1 for reasons of convenience, and the iodide concentration is calculated to react with a maximum 2.0 mg/l Cl_2. The difference in initial and final iodide concentrations is caused both by reaction of the iodide with chlorine, by dilution of the reagent with sample. A blank determination is made by diluting the reagent with redistilled water and taking initial and final electrode readings.

The original Cl_2 concentration can be determined by calculation with knowledge of the change in iodide concentration, the dilution effect, and the original sample volume, but the tremendous utility of this method lies in the fact that Cl_2 concentration can be correlated with the actual change in electrode potential. The changes in electrode potential which are measured are as follows:

$\Delta E = E - E_s$ = change in electrode potential for addition of reagent to sample (6.6)

$\gamma = E - E'$ = change in electrode potential for addition of reagent to distilled water (6.7)

$\Delta E_c = E - \gamma$ = change in electrode potential corrected for dilution effects (6.8)

where:

E = electrode potential in iodide reagent (mv)

E' = electrode potential in reagent-distilled water solution (mv)

E_s = electrode potential in reagent-sample solution (mv)

If γ can be made constant by controlling temperature, reagent composition, and the reagent-to-sample volume ratio, a permanent calibration curve can be constructed relating ΔE_c or ΔE to mg/l Cl_2.

6.3 EXPERIMENTAL

6.31 MATERIALS AND METHODS

Capital Controls Analyzer

The basic purpose of this study was to compare data obtained with the Analyzer with those obtained with a Wallace and Tiernan (W&T) amperometric titrator, which was accepted as the standard. The sample line on the Analyzer was connected either to a tap water line or to a gravity-fed 5 gallon Nalgene Carboy in which synthetic solutions were prepared. The calibration procedure, proposed by Capital Controls, Inc., is as follows: shorting of the recorder leads and mechanically zeroing the recorder, running a solution through the Analyzer and determining its chlorine content with a W&T titrator, and adjustment of a potentiometer on the Analyzer to equilibrate the recorder with the titrator. A modification of this procedure was used in the accuracy studies. Two solutions of chlorine, with concentrations toward either end of a 0 - 1.0 mg/l concentration range, were used to check the linearity of the calibration. Synthetic solutions were prepared with commercial bleach in which chlorine was in the sodium hypochlorite form.

Orion Electrode Method[32]

The reagent was prepared by diluting $1.128 \times 10^{-3}M$ KI 1:20 at the time of use with a solution of $1.052 \times 10^{-1}M$ acetic acid, $1.052 \times 10^{-1}M$ sodium acetate, and $1.052 \times 10^{-3}M$ sodium citrate. Analytical Reagent grade chemicals were used. Accurately diluted samples of tap water or chlorine bleach were used to obtain relative data on accuracy. Before each set of standard dilutions was run, a blank correction with distilled water was made. Each dilution was made immediately before the particular sample was run to equalize the adsorption of chlorine onto the glass (which is a function of concentration) in each sample. The reagent concentration was determined with an iodide selective ion electrode (Orion Model 94-53), the sample added, and the final electrode potential read. The potentials were converted to iodide concentrations with a previously constructed calibration curve, and calculations were made to determine the original chlorine concentration.

6.32 RESULTS AND DISCUSSION

Capital Controls Analyzer

The Analyzer was placed on a tap water stream for several days in order to observe its operation without any calibration. Variations were observed in the free residual chlorine concentration, especially during hours when the laboratory was occupied (Fig. 6-2). The overflow weir ensures that these variations are not a function of water flow variations directly (assuming a constantly excess supply), but are due to: (1) losses or disruptions in residual chlorine from building water use, or (2) changes in parameters other than residual chlorine which effect the cell calibration.

To study changes in parameters which affect calibration, a synthetic sample of deionized water was prepared containing approximately the same free chlorine concentration as tap water at the time of the experiment. Portions of the synthetic sample were run through the Analyzer alternately with tap water, allowing time for the Analyzer to equilibrate in each sample before readings were taken. The free chlorine content of the synthetic sample and the tap water were within ± 5% of 0.9 mg/l throughout the entire experiment. Although the tap and synthetic water samples contained the same chlorine according to the titrator, the Capital Controls Analyzer showed the synthetic sample to contain about 0.35 mg/l more chlorine than the tap water. This indicates that the general character of the water being measured has a significant effect on the Analyzer calibration. Therefore, calibration must be made in each particular water supply to be monitored. However, later experiments

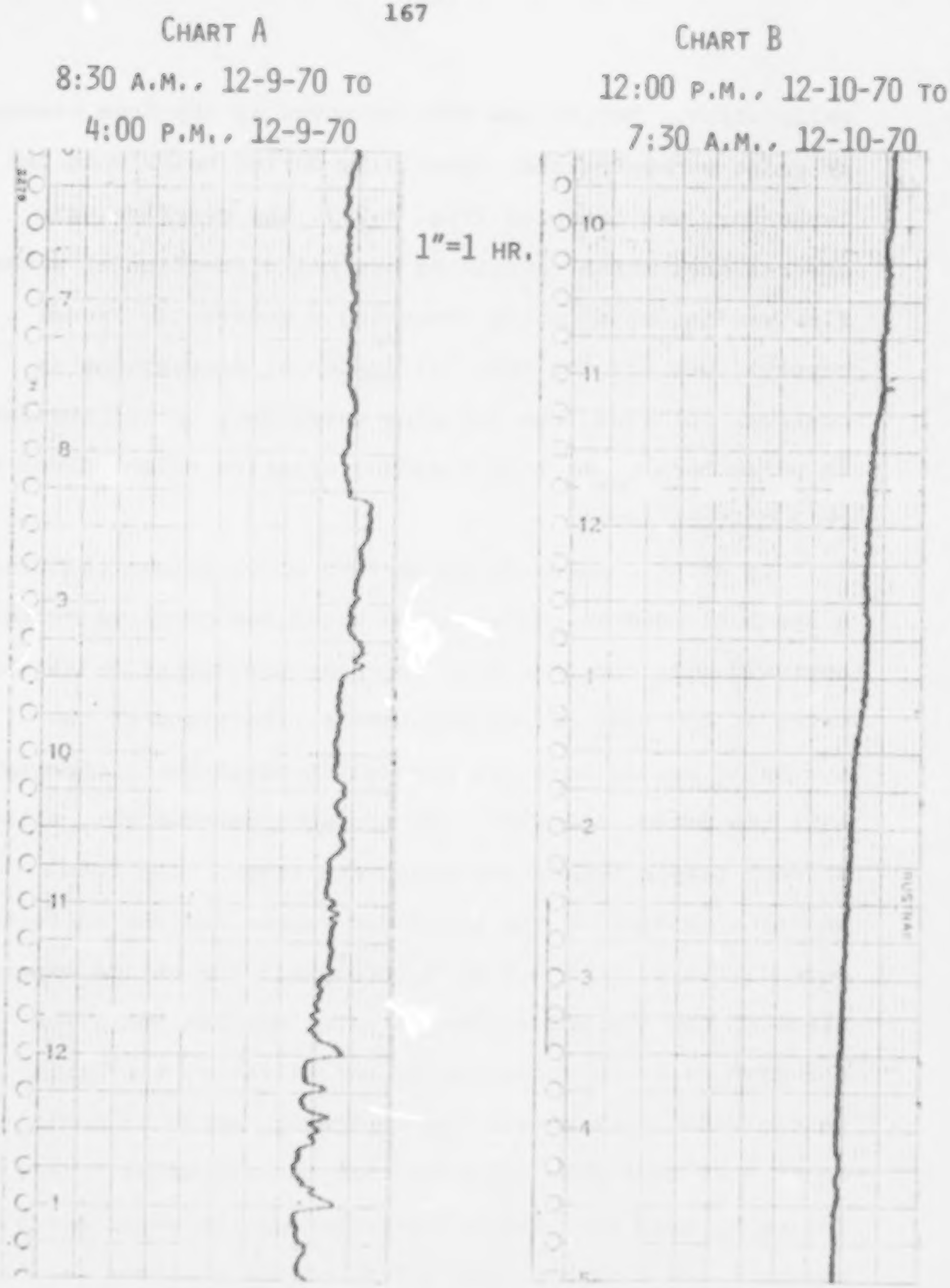


CHART A
8:30 A.M., 12-9-70 TO
4:00 P.M., 12-9-70

CHART B
12:00 P.M., 12-10-70 TO
7:30 A.M., 12-10-70

FIGURE 6-2. SAMPLE RECORDER OUTPUT OF CAPITAL CONTROLS ANALYZER

in which Analyzer readings were compared to amperometric titrations revealed that minor variations in a single water supply's character do not affect the calibration significantly and that variations seen in Fig. 6-2 were indeed caused by changes in free chlorine content. The accuracy of calibration was investigated next.

The Capital Controls procedure of calibration was followed by mechanically zeroing the recorder. Two solutions were then prepared in deionized water, one of about 0.8 mg/l free chlorine and one, about 0.2 mg/l free chlorine, then measured exactly by the titrator. These solutions were run through the Analyzer in sequence, with samples taken periodically and checked by the titrator to ensure constancy of concentration. It was possible with one setting of the potentiometer to calibrate the Analyzer to read both solutions exactly. The only limitations on accuracy were the sizes of the recorder stylus and chart paper. These experiments were duplicated many times and the results were the same.

Orion Electrode Method

Various experiments were made to determine the accuracy as well as problems associated with this method. The first experiment was a set of potentiometric titrations of chlorine solutions with iodide to determine the rapidity and nature of the chlorine-iodide reaction. Four different types of solutions were titrated at both pH = 4 and 7:

chlorine standards made with commercial bleach, tap water, tap water spiked with chlorine standard, and tap water spiked with chlorine standard to which a few drops of NH_4OH were added. Results are shown in Figs. 6-3 through 6-6.

The effect of pH on the chlorine-iodide reaction can be seen by comparing the "A" graph to the "B" graph of each figure. In each case, the chlorine concentration of the sample titrated at pH = 4 appears greater than that at pH = 7. This is because at pH = 4, both free and combined chlorine react quantitatively with I^-, but at pH = 7 only the free chlorine reacts quantitatively while the combined chlorine reacts slowly and non-quantitatively. Therefore, the difference in chlorine concentration between "B" and "A" represents roughly the combined chlorine in the sample.

The increase in chlorine concentration due to spiking of the tap water is apparent in comparing Fig. 6-5A with 6-4A, and 6-5B with 6-4B. The spiking was qualitative, so the actual concentration differences are not significant; the general effect is.

Finally, the combination effect of NH_4OH with chlorine is displayed by comparing Figs. 6-6A and 6-6B. A few drops of NH_4OH were added to both samples to combine with free chlorine. Whether mono- or dichloramines were the actual species formed is uncertain, but the titration at pH = 4 showed the anticipated level of total chlorine. At pH = 7,

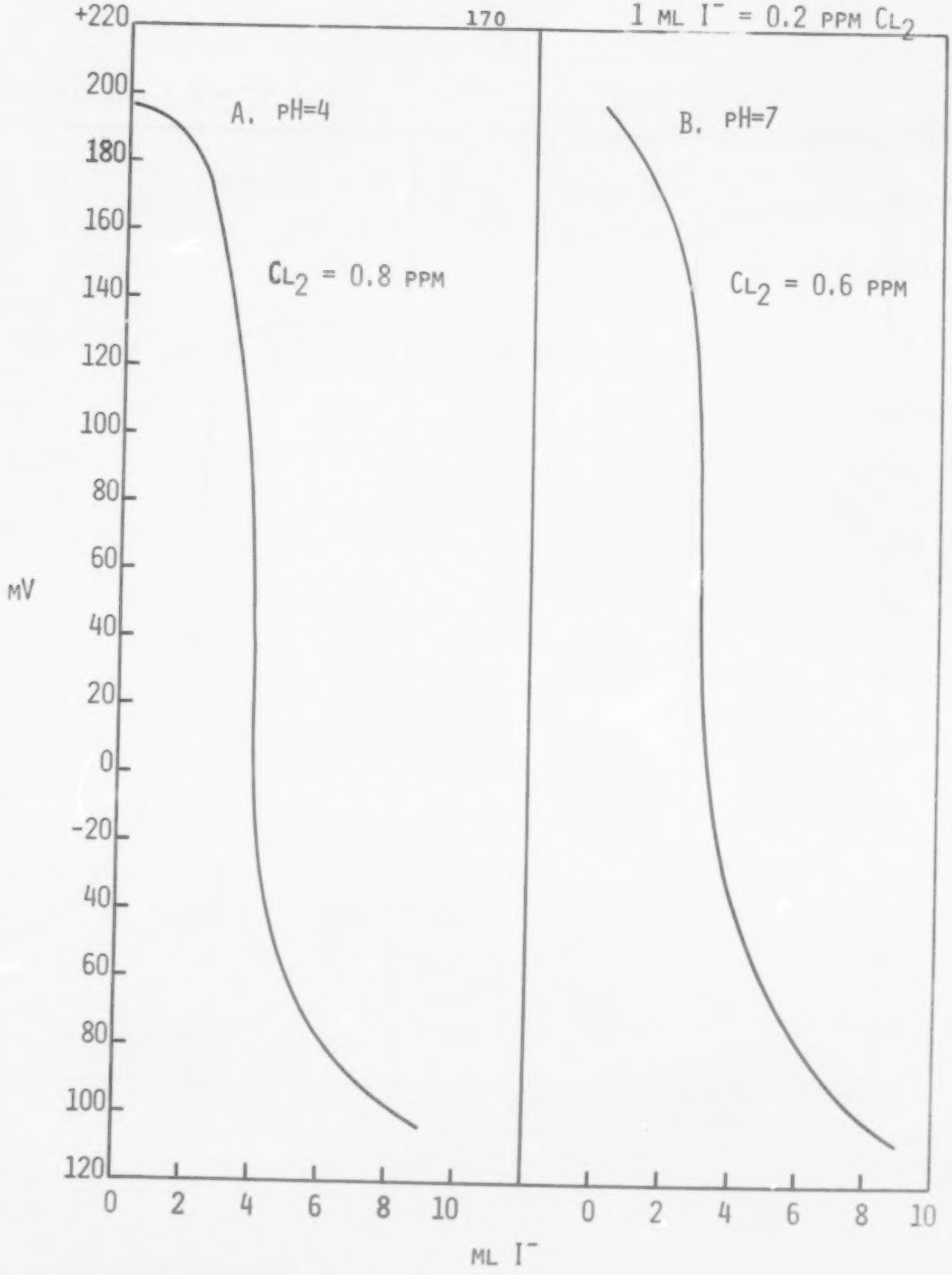


FIGURE 6-3. POTENTIOMETRIC TITRATION OF A SYNTHETIC CHLORINE SOLUTION WITH IODIDE

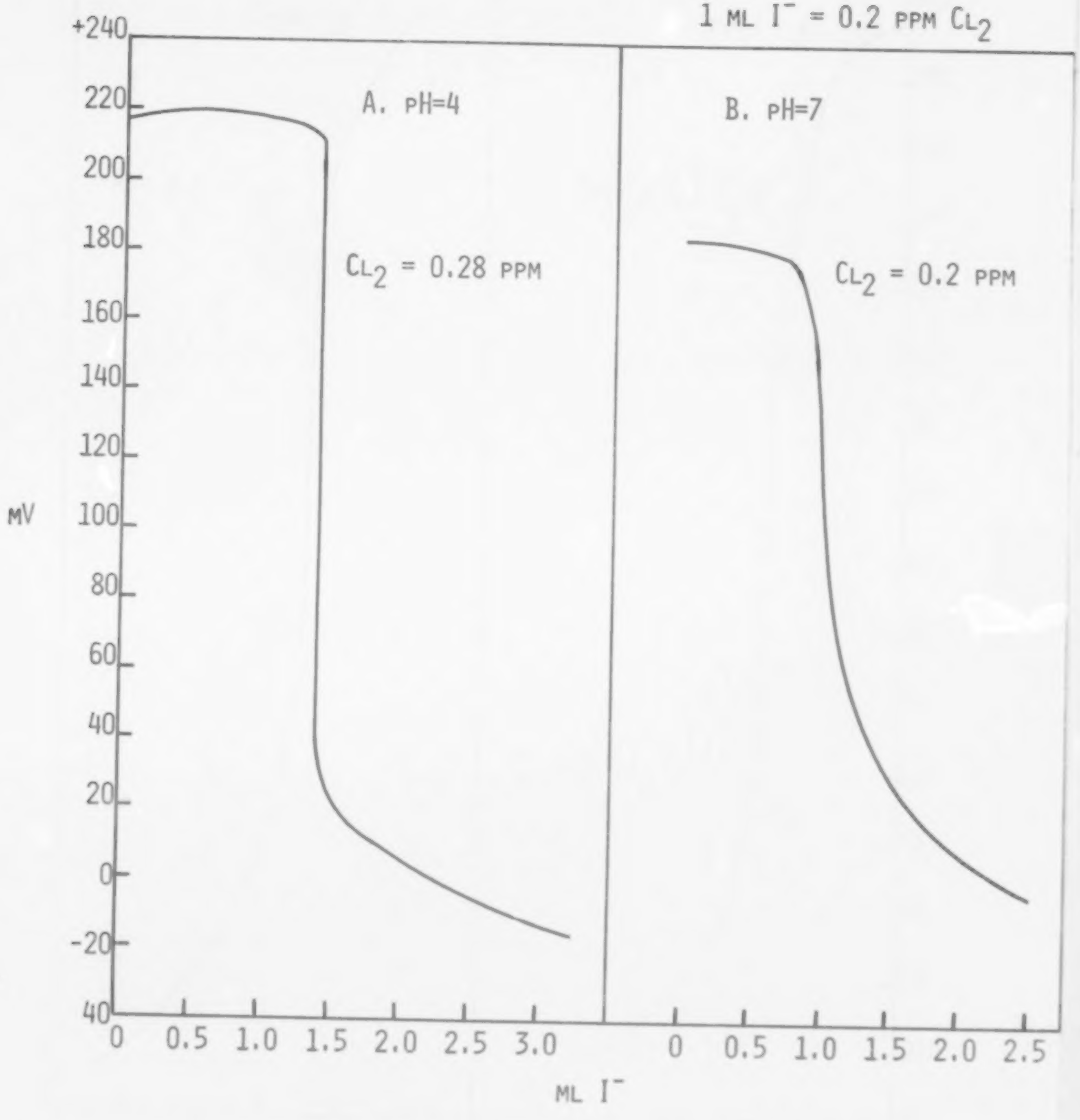


FIGURE 6-4. POTENTIOMETRIC TITRATION OF TAP WATER WITH I^-

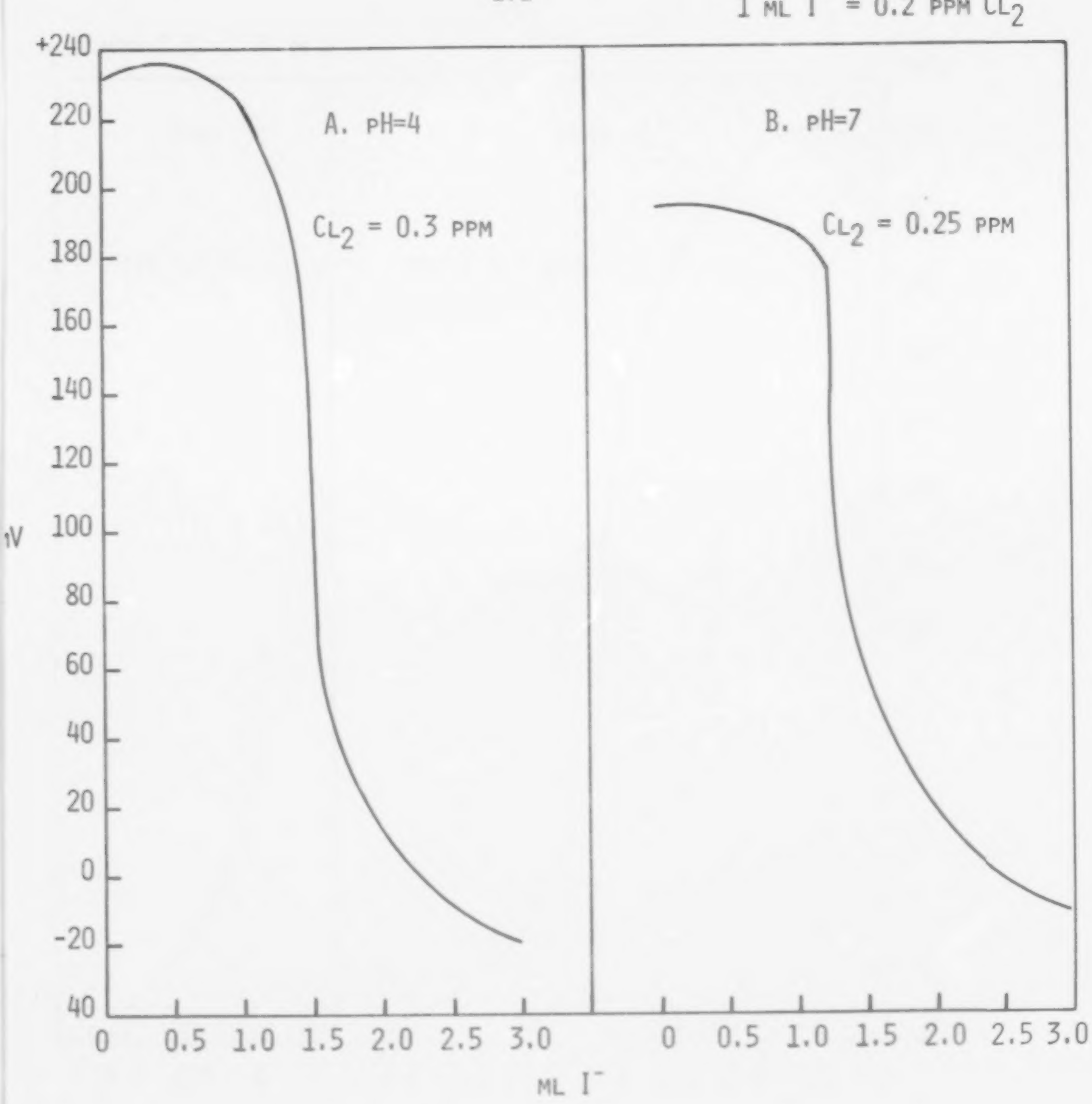


FIGURE 6-5. POTENTIOMETRIC TITRATION OF CHLORINE - SPIKED TAP WATER WITH I^-

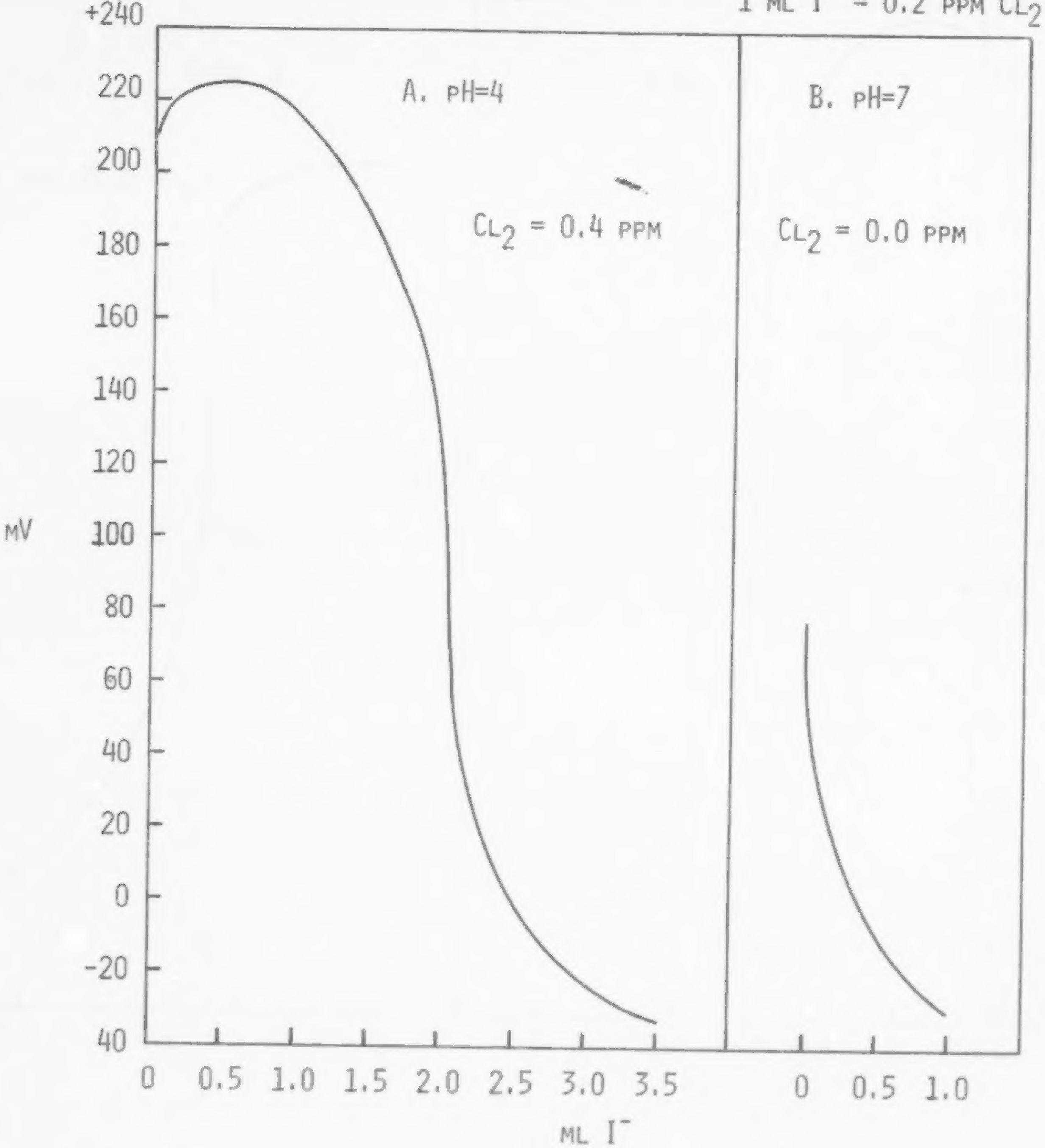


FIGURE 6-6. POTENTIOMETRIC TITRATION OF CHLORINE - SPIKED TAP WATER + NH_4OH WITH I^-

there was no free residual chlorine.

To study the accuracy of this method, relative standards were prepared by accurately diluting a bleach solution of unknown concentration. Chlorine concentrations were determined by calculating the actual iodide lost with an electrode calibration curve, and calculating the amount of chlorine that had to be present to consume this iodide, taking into account the dilution factor γ. For the plot shown in Fig. 6-7, the value of γ determined at the beginning of the experiment was 16.6 mv. Fig. 6-7 shows the relative accuracy of the method by the linearity of the curve. The reason the curve does not go through the origin as it should is that the blank γ was determined incorrectly. The correct value of γ can be determined by plotting ΔE (uncorrected) vs. the percent of stock solution; γ is then the value at the y-intercept where percent of stock solution equals zero and ΔE is due to dilution. When this correction of γ is made, the curve of Fig. 6-7 will then pass through the origin. It is therefore established that the electrode method is quite accurate in batch solutions if the correct value of γ is used.

Automation of this method is theoretically accomplished by the apparatus shown in Fig. 6-8. The proportioning pump regulates a pre-determined ratio of reagent-to-sample. Electrode R measures a relatively constant concentration of I^- in the reagent buffer and electrode T measures the

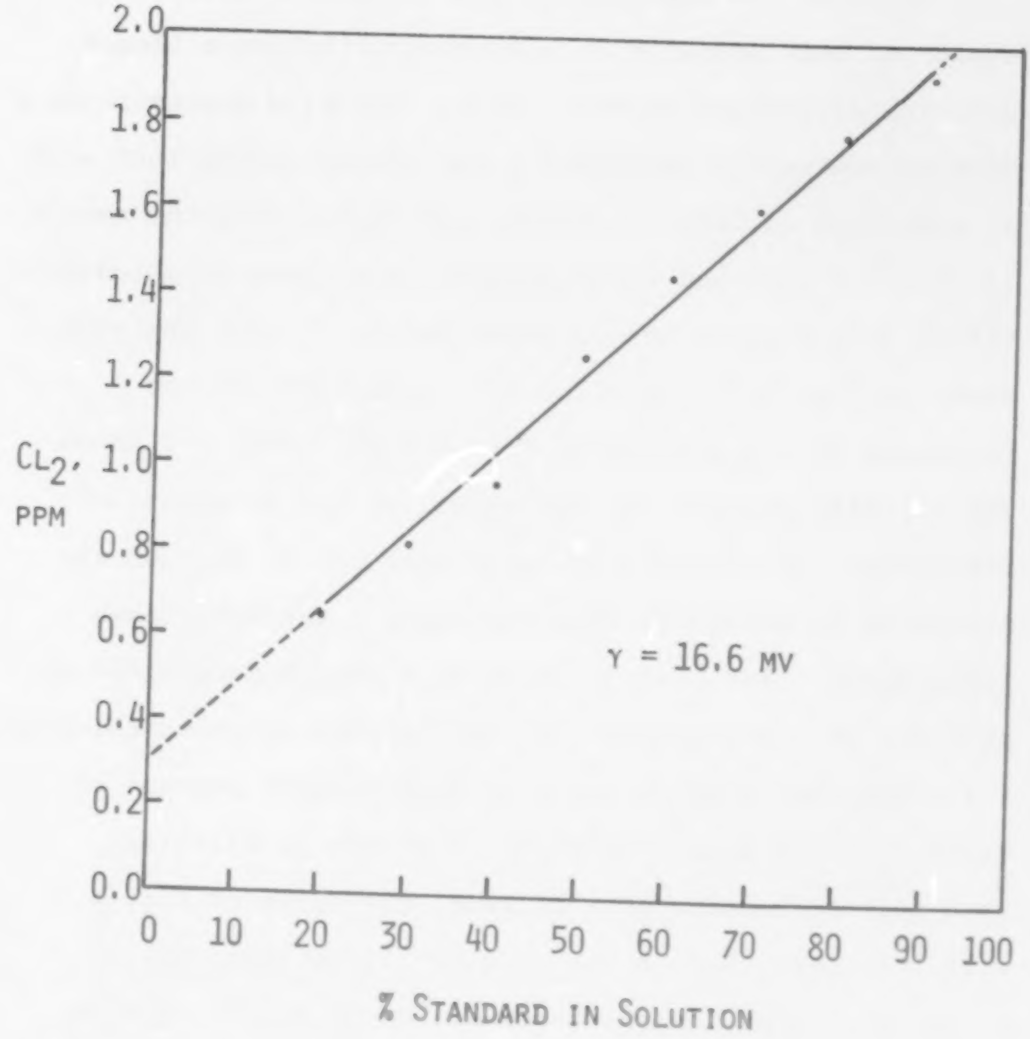


FIGURE 6-7. ION SELECTIVE ELECTRODE METHOD - % STANDARD IN SOLUTION VS. $[Cl_2]$

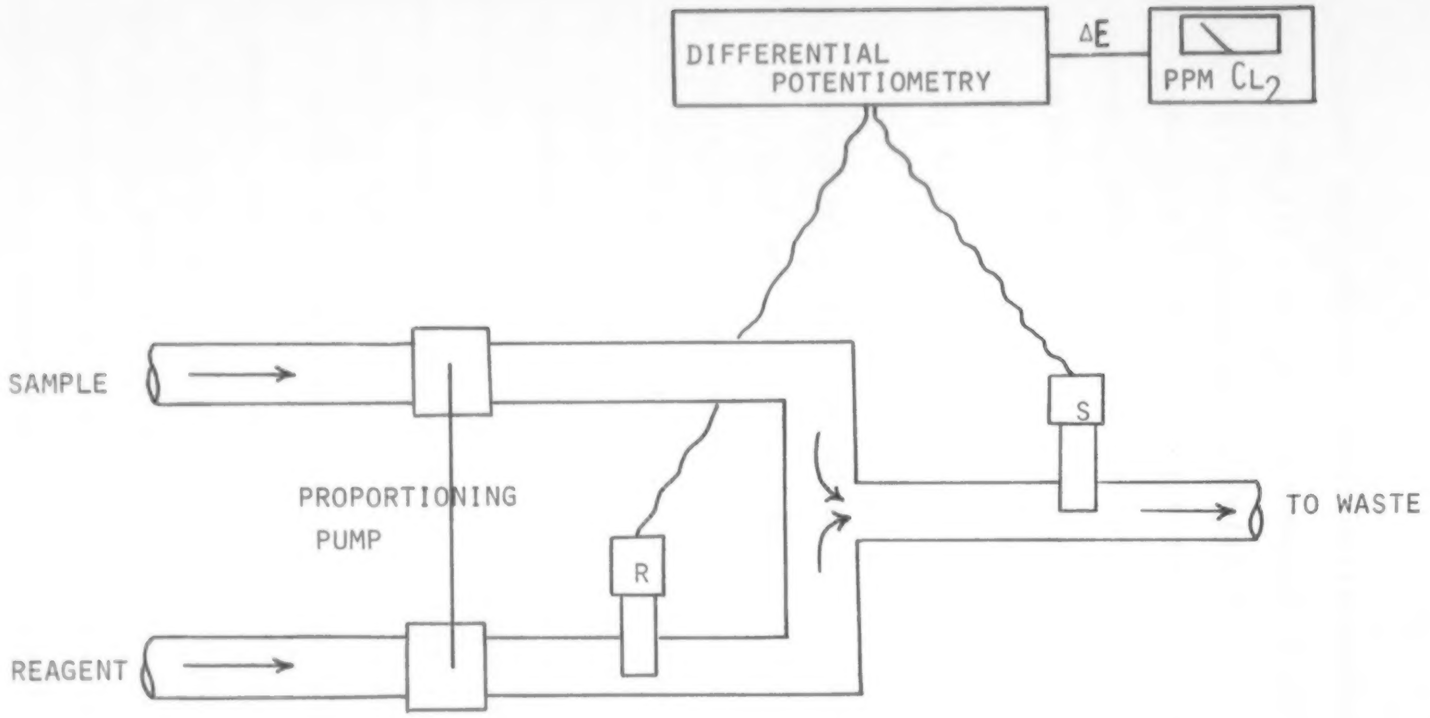


FIGURE 6-8. FLOW SYSTEM FOR AUTOMATION OF ION SELECTIVE ELECTRODE METHOD[32]

variable I^- concentration after reaction with chlorine in the sample. The difference $E_R - E_T$ (mv) can be calculated with differential potentiometry equipment, and calibrated in terms of mg/l Cl_2 for visual readout. A pre-determined blank γ should be included in the calibration. Potential problems associated with automation are: determination of an accurate γ, required accuracy in proportioning reagent and sample, the amount of reagent required, and stability of the reagent.

The proportioning problem can easily be overcome with an accurate perstaltic pump. However, the dilute solution of iodide is very unstable, subject to air oxidation, and must be prepared daily by diluting a concentrated iodide solution with acetate buffer. This is not desirable in a continuous monitor so a concentrated iodide-buffer solution must be used to ensure stability, as well as to reduce the reagent volume needed. If a concentrated reagent is used, the reagent-to-sample ratio is reduced proportionately, from 1:1 to 1:19, for example. The dilution factor γ (mv) is increased, but the range of ΔE_c (mv) is not changed at all, so no accuracy in the electrode readings is lost. However, when a concentrated reagent is used, slight errors in proportioning cause much greater errors in readout.

The major inaccuracy in this method is in determination of an accurate and stable dilution factor γ, as can be seen from the previously described experiment. During numerous batch experiments, γ was determined on different dilutions of the same concentrated stock solutions, and variations from 15.0 to 21.0 mv were found. The most common γ was about 16.5 mv. Because ΔE_c has a range of 17 mv for chlorine concentrations of 0 - 1.0 mg/l Cl_2, an error of 4 mv in γ can be quite significant. It is likely that a stable γ can be obtained for a large volume of concentrated reagent, but it would probably vary for each batch. This need for flexibility must be considered in designing the differential potentiometry and visual readout apparatus.

6.4 SUMMARY

It has been demonstrated that both the Capital Controls Residual Chlorine Analyzer and the Orion selective ion electrode method are capable of achieving good accuracy in the measurement of residual chlorine in potable water.

7.0 TURBIDITY

7.1 GENERAL

One of the most fundamental yet important water quality parameters to be monitored in a distribution system is turbidity. According to the Public Health Service[16], turbidity is not so much a measure of drinking water safety as aesthetic acceptability. Experience has shown that when the limit of five Jackson Turbidity Units (JTU) is exceeded, water is aesthetically objectionable to the consumer and alternate, possibly less safe, supplies may be used. Thus, a distribution system monitor should include a continuous turbidimeter to measure changes in turbidity caused by corroding mains and cross-connections. To date, only the Hach Low Range Continuous Flow Turbidimeter, Model 1720, has been evaluated in terms of its feasibility for potable water monitoring applications.

7.2 THEORY

The Hach Model 1720 is a photoelectric turbidimeter which operates on the nephelometric, or light scattering, principle. A photocell is positioned at a 90° angle to the light path to detect the amount of light that is scattered by turbidity. There are three major advantages to the nephelometer when compared with an absorptometer (an instrument in which light is passed through the sample cell and a photocell at the opposite side of the sample cell detects the amount of light that is not absorbed or scattered): (1) The nephelometer is much more sensitive to low turbidities because it measures a relatively small amount of light; (2) The nephelometer shows a direct response - the photocell signal increases with increasing turbidity rather than decreasing with increasing turbidity as in the absorptometer (this simplifies calibration); and (3) Most importantly, the nephelometer does not detect color as turbidity, whereas the absorptometer does.

7.3 EXPERIMENTAL

7.31 MATERIALS AND METHODS

The entire turbidity monitoring assembly consists of the Continuous Flow Turbidimeter, a bubble trap installed upstream from the turbidimeter, a Hach Master Indicator readout meter, and a Rustrak Model 288 recorder. (All equipment, except the bubble trap, was consigned to the project by the Hach Chemical Company, Ames, Iowa.) Fig. 7-1 shows a cut-away drawing of the turbidimeter unit[36]. The bubble trap was constructed of Plexiglass and installed in a manner similar to that shown schematically in Fig. 7-2.[36] The entire assembly was installed on a tap water line and operated continuously for approximately three months.

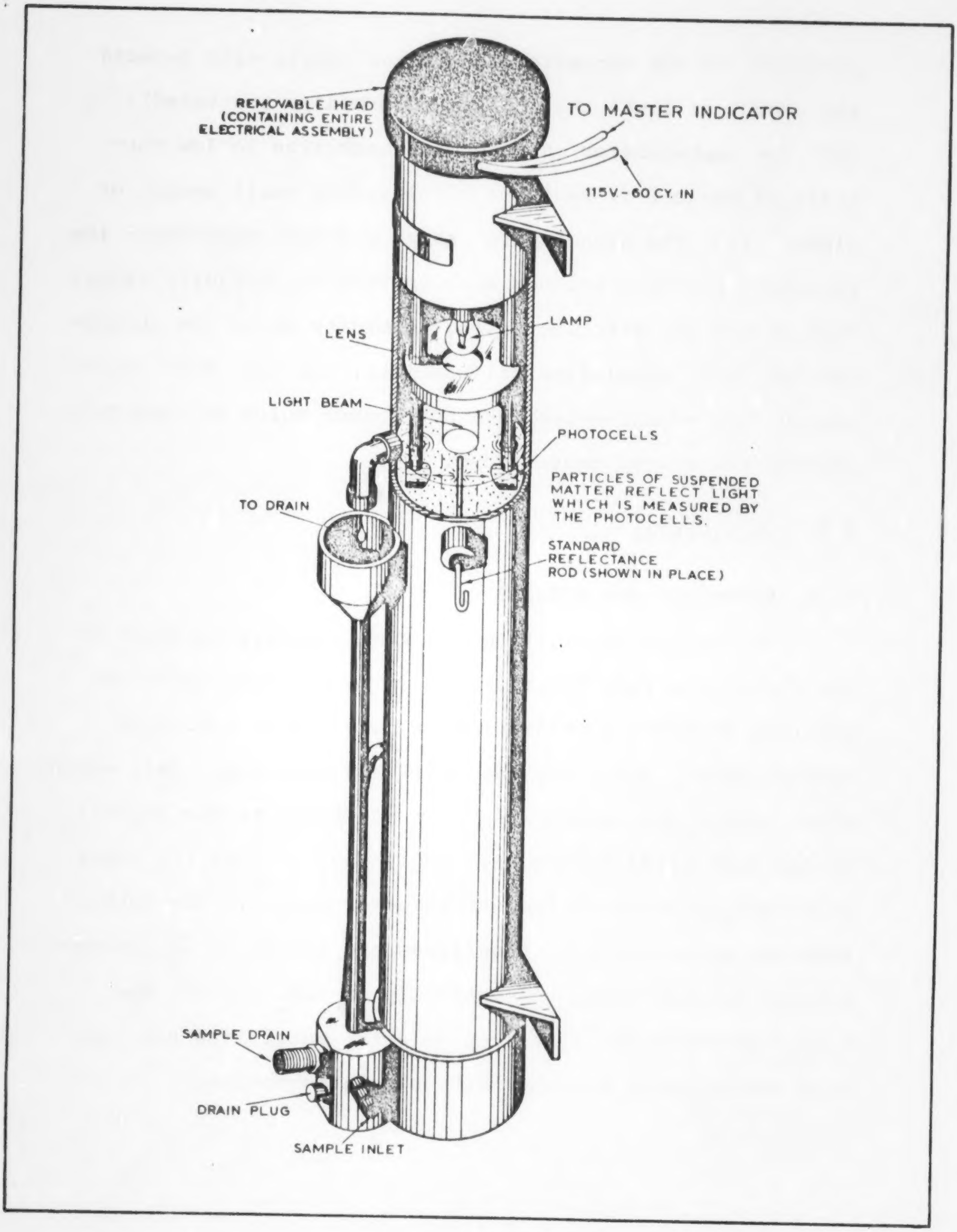


Figure 7-1. Cut-away view of the Hach CR Low Range Turbidimeter Model 1720[36]

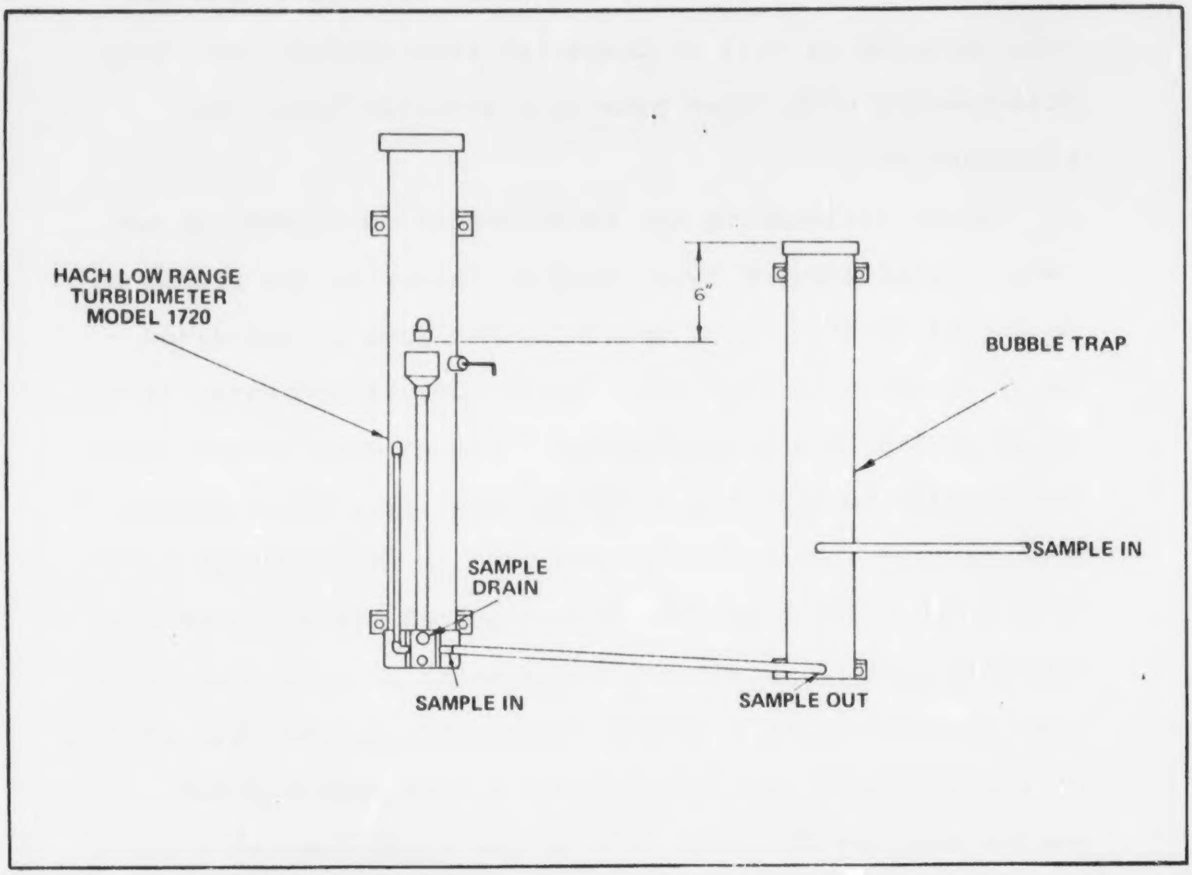


Figure 7-2. Schematic of turbidimeter-bubble trap assembly[36]

7.32 RESULTS AND DISCUSSION

Major emphasis in the evaluation of the Hach Turbidimeter was on determining required frequency of maintenance and recalibration as well as comparing flow-through turbidity measurements with those made on a standard laboratory turbidimeter.

After calibrating the turbidimeter on-stream, it was recalibrated once or twice weekly, following the procedure described by Hach using specially designed standardized rods, as shown in Fig. 7-1. Weekly checks indicated little or no shifts in the calibration. The standard reflectance rod is made to effect a 5 JTU increase over the original reading, and observed increases were in the order of 4.7 to 5.0 JTU. The observed error required little correction for elimination. After the first month of operation, even less correction was required, presumably because the surface of the photocell was "acclimated" to the sample water during that period. The life of the light source is estimated by the manufacturer to be approximately one year. The unit being used in this study has not been on-stream long enough to verify this estimate. Fouling of the photocells is not expected to occur in tap water monitoring applications, thus frequent maintenance will not be required.

Accuracy comparisons were made in the laboratory at levels of 1-30 JTU's, using a laboratory turbidimeter. Results were identical.

7.4 SUMMARY

As a commercially available, continuous turbidimeter, the Hach Model 1720 appears to be useful for potable water monitoring applications. Maintenance and recalibration requirements are equal to or better than other systems being considered for the monitor. Accuracy is essentially 100 percent when compared with data obtained with a laboratory turbidimeter.

8.0 FUTURE WORK

Specific aims during the current phase of this project include:

- design a prototype system for monitoring the following water quality parameters:

Parameter	Sensor Type
1. Temperature	Thermistor
2. Dissolved Oxygen	Voltammetric Membrane Electrode
3. Electrical Conductance	A-C Conductance Cell
4. pH	Glass Electrode
5. Turbidity	Light Scattering
6. Residual Chlorine (Free & Total)	Automated Amperometric
7. Gross Organic Matter	UV Absorption Spectrophotometry
8. Nitrates	Ion Selective Electrodes
9. Fluorides (Free & Total)	Ion Selective Electrodes
10.	
10. Hardness	Ion Selective Electrodes
11. Chlorides	Ion Selective Electrodes
12. Trace Metals (Cu, Pb, Cd, Zn)	Anodic Stripping Voltammetry (ASV)
13. Stability	Electrochemical Calcium Carbonate Deposition (ECCD)

- on-stream evaluation of the prototype model
- develop a comprehensive maintenance schedule in

preparation for further evaluation of the model under field conditions

- continue to study the calcium carbonate deposition test and establish its feasibility for monitoring stability
- automate the ASV technique for measuring trace metals
- evaluate techniques for on-stream monitoring of alkalinity
- evaluate commercially available corrosion meters for applicability to continuous monitoring systems

Long term goals include completion of all objectives and priorities established for the project including field evaluation in distribution systems of major cities which have expressed an interest in monitoring the quality of potable water supplies.

9.0 REFERENCES

1. Eisenman, G. "Theory of Membrane Electrode Potentials: An Examination of the Parameters Determining the Selectivity of Solid and Liquid Ion Exchangers and of Neutral Ion-Sequestering Molecules," Ion-Selective Electrodes, ed. by Durst, R.A. Department of Commerce, National Bureau of Standards Special Publication 314, 1969.

2. Instruction Manual, Halide Electrodes. Orion Research Incorporated, Cambridge, Massachusetts, 1967.

3. Durfor, C.N., and Becker, E. Public Water Supplies of the 100 Largest Cities in the United States, 1962. United States Geological Survey Water Supply Paper 1812, 1964.

4. Baker, M.N. "In Quest of Pure Water," Journal American Water Works Association, 40, 527, (1948).

5. American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 12th Edition. New York: American Public Health Association, 1966.

6. Instruction Manual, Divalent Cation Electrode. Orion Research Incorporated, Cambridge, Massachusetts, 1967.

7. Brand, M.J.D., and Rechnitz, G.A. "Differential Potentiometry with Ion-Selective Electrodes," Analytical Chemistry, 42:6, 616, (1970).

8. Oliver, R.T., and Mannion, R.F. Ion-Exchange Electrodes in Process Control: Water Hardness Measurement of Ion Exchange Treated Water. Presented at the 16th National Symposium of the Instrument Society of America, Analysis Instrument Division, May 25-27, 1970.

9. Panel Discussion. "The Health Effects of Nitrates in Water," Proceedings 12th Sanitary Engineering Conference. Urbana, Illinois: University of Illinois, 1970.

10. Instruction Manual, Nitrate Electrode, 1st and 2nd Editions. Orion Research Incorporated, Cambridge, Massachusetts, 1967 and 1970.

11. Potterton, S., and Shults, W.D. "An Evaluation of the Performance of the Nitrate-Selective Electrode," *Analytical Letters*, *1*:2, 11, (1967).

12. Langmuir, R., and Jacobsen, R.L. "Specific-Ion Electrode Determination of Nitrate in Some Fresh Waters and Sewage Effluents," *Environmental Science and Technology*, *4*, 10, (Oct. 1970).

13. Schneider, C. Personal communication, 1970.

14. Paul, J.L., and Carlson, R.M. "Nitrate Determination in Plant Extracts by the Nitrate Electrode," *Journal Agriculture and Food Chemistry*, *16*:5, 766, (1968).

15. *Newsletter/Specific Ion Electrode Technology*. Orion Research Incorporated, Cambridge, Massachusetts, Sept./Oct. 1970.

16. *Public Health Service Drinking Water Standards*. United States Department of Health, Education, and Welfare, Public Health Service, 1962.

17. Larson, T.E., and Skold, R.V. "Corrosion and Tuberculation of Cast Iron," *Journal American Water Works Association*, 49, 1294, (1957).

18. Stumm, W. "Estimating Corrosion Rates in Water," *Industrial and Engineering Chemistry*, *51*, 1487, (1959).

19. Mancy, K.H. "Dissolved Oxygen - A Corrosion Inhibitor or Promoter in Water Distribution System," *Proceedings National Association of Corrosion Engineers*. Boston, Massachusetts, Oct. 1966.

20. McClanahan, M.A. Ph.D. Thesis, The University of Michigan, 1968.

21. Langelier, W.F. "The Analytical Control of Anti-Corrosion Water Treatment," *Journal American Water* Works Association, *28*, 1500, (1936).

22. Larson, T.E., and Buswell, A.M. "Calcium Carbonate Saturation Index and Alkalinity Interpretations," *Journal American Water Works Association*, 34, 1664, (1942).

23. Ryzner, J.W. "A New Index for Determining the Amount of Calcium Carbonate Scale Formed by a Water," *Journal American Water Works Association*, *36*, 472, (1944).

24. Pytkowicz, R.M. "Rates of Inorganic Calcium Carbonate Nucleation," Journal Geology, 73, 196, (1965).

25. Weyl, P.K. "Solution Kinetics of Calcite," Journal Geology, 66, 163, (1958).

26. Weyl, P.K. "The Carbonate Saturometer," Journal Geology, 69, 32, (1961).

27. Enslow, L.H. "The Continuous Stability Indicator," Water and Sewerage Works, 107, (March 1939).

28. Enslow, L.H. "The Continuous Stability Indicator and the Langelier Index," Water and Sewerage Works, 283, (July 1939).

29. Peterson, T.L., Brant, D.O., and Mancy, K.H. "Characterization of Trace Metals in Municipal Water Supplies by Thin Layer Anodic Stripping Voltammetry". Presented at 160th National Meeting of the American Chemical Society. Chicago, Illinois, September 1970.

30. Operation Manual, Aqua Test Water Quality Monitor. Aqua Test Corporation, Arlington, Massachusetts.

31. Dobbs, R.A., Wise, R.H., and Dean, R.B. "The Use of Ultraviolet Absorbance for Monitoring the Total Organic Carbon Content of Water and Wastewater." United States Department of the Interior, Federal Water Pollution Control Administration, Advanced Waste Treatment Research Laboratory. Cincinnati, Ohio, May 1969.

32. Newsletter/Specific Ion Electrode Technology. Orion Research Incorporated, Cambridge, Massachusetts, May/June, 1970.

33. Instruction Manual, Capital Controls Residual Chlorine Analyzer. Capital Controls, Incorporated, Colmar, Pennsylvania, 1970.

34. Stenberg, N.K. Personal communication, 1971.

35. Instruction Manual, Wallace and Tiernan Amperometric Titrator, Instruction Book #WIA 790-1-2, Wallace and Tiernan Incorporated, Industrial Products Division, Belleville, New Jersey.

36. Instruction Manual, Hach CR Low Range Turbidimeter Model 1720. Hach Chemical Company, Ames, Iowa.

ACKNOWLEDGEMENTS

This study was supported in part by Division of Water Hygiene, EPA, Research Grants No. 1 R01 EC 00318-01 and -02.

The cooperation of the following manufacturers and agencies who have consigned equipment to the project is gratefully acknowledged:

Aqua Test Corporation
Capital Controls Company, Inc.
City of Chicago
Hach Chemical Company
Schneider Instrument Company
Van Waters & Rogers Scientific Company

The project staff wishes to express its appreciation to the members of the Technical Advisory Committee for contributing their expertise to this project.